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**(54) ORGANIC ELECTROLUMINESCENT ELEMENT**

(57) An organic electroluminescence device which exhibits an excellent purity of color and a high efficiency of light emission, has a long life and emits reddish light and a novel compound having these characteristics are provided.

The organic electroluminescence device comprises an organic layer disposed between at least one pair of electrodes, wherein the organic layer comprises a compound having a fluoranthene skeleton structure substituted at least with an amine group or an alkenyl group.

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## DESCRIPTION

### ORGANIC ELECTROLUMINESCENCE DEVICE

#### TECHNICAL FIELD

The present invention relates to an organic electroluminescence device which is used as a light source such as a planar light emitting member of televisions and a back light of displays, exhibits an excellent purity of color and a high efficiency of light emission, has a long life and emits reddish light and to a novel compound having these characteristics.

#### BACKGROUND ART

Electroluminescence (referred to as EL, hereinafter) devices using organic compounds are expected to be used for inexpensive full color display devices of the solid light emission type which can display a large area and development thereof has been actively conducted. In general, an EL device is constituted with a light emitting layer and a pair of electrodes faced to each other at both sides of the light emitting layer. When a voltage is applied between the electrodes, electrons are injected at the side of the cathode and holes are injected at the side of the anode. The electrons are combined with the holes in the light emitting layer and an excited state is formed. When the excited state returns to the normal state, the energy is emitted as light.

Although the practical application of organic EL devices has started recently, devices for full color displays are still under development. In particular, a material for organic EL devices which exhibits an excellent

purity of color and a high efficiency of light emission, has a long life and emits reddish light has been desired.

In an attempt to satisfy the above desire, a device emitting red light in which a derivative of naphthacene or pentacene is added to a light emitting layer is disclosed in Japanese Patent Application Laid-Open No. Heisei 8(1996)-311442. Although this device exhibits an excellent purity of red light, the device exhibits an efficiency of light emission as low as 0.7 lm/W and has an insufficient average life which is shorter than 150 hours. An average life of at least several thousand hours is necessary for practical applications. A device in which a compound derived from dicyanomethylene (DCM) is added to a light emitting layer is disclosed in Japanese Patent Application Laid-Open No. Heisei 3(1991)-162481. However, this device exhibits an insufficient purity of red light. In Japanese Patent Application Laid-Open Nos. Heisei 10(1998)-340782 and Heisei 11(1999)-40360, organic EL devices using fluoranthene compounds are disclosed. However, the devices using the compounds disclosed in the above patent applications do not emit yellow to red light. The efficiency of light emission is as small as 4 cd/A or smaller and insufficient.

#### DISCLOSURE OF THE INVENTION

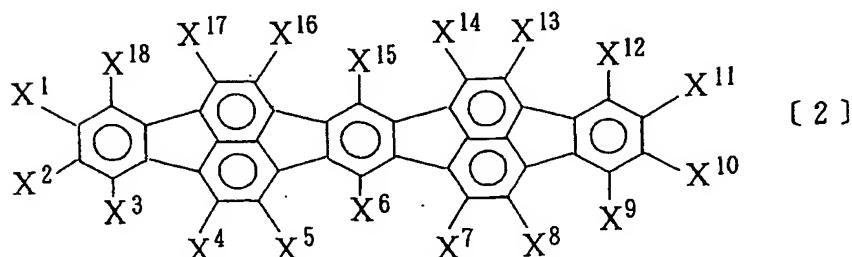
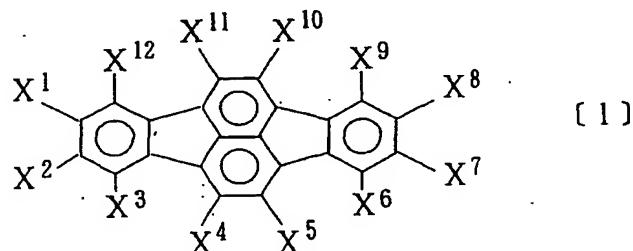
The present invention has been made to overcome the above problems and has an object of providing an organic EL device which exhibits an excellent purity of color and a high efficiency of light emission, has a long life and emits reddish light and a novel compound having these characteristics.

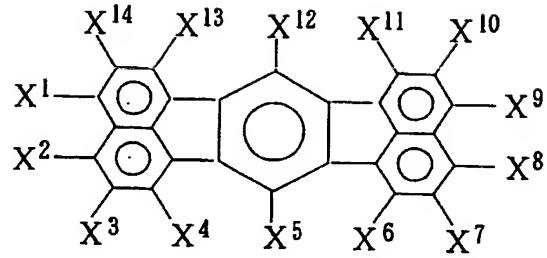
As the result of extensive studies by the present inventors to develop

an organic electroluminescence device (referred to as an organic EL device, hereinafter) having the above advantageous properties, it was found that the object can be achieved by using a compound having a fluoranthene skeleton structure substituted at least with an amine group or an alkenyl group as the light emitting material.

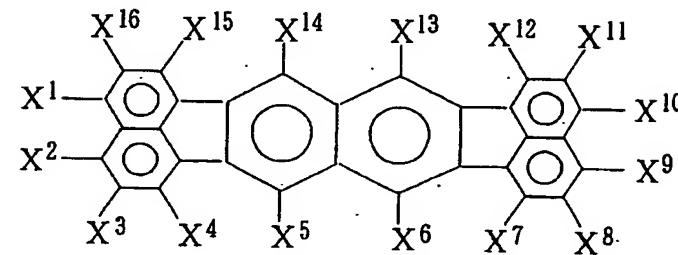
The organic electroluminescence device of the present invention comprises an organic layer disposed between at least one pair of electrodes, wherein the organic layer comprises a compound having a fluoranthene skeleton structure substituted at least with an amine group or an alkenyl group.

It is preferable that the above compound is a compound selected from compounds represented by the following general formulae [1] to [18]:

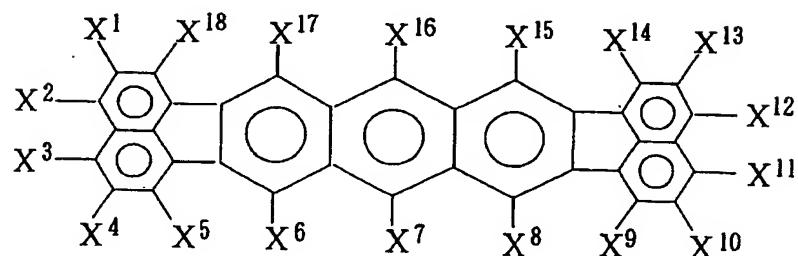




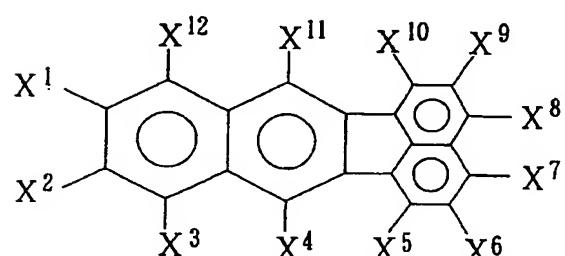
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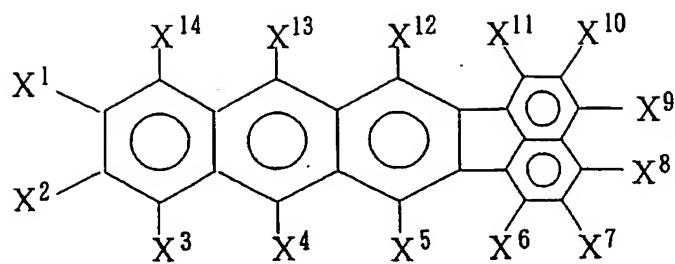
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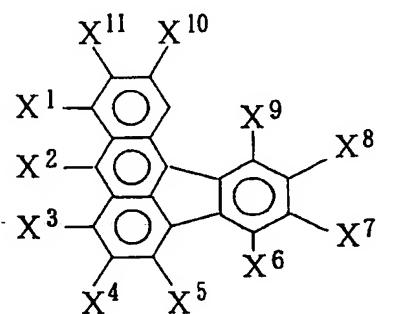
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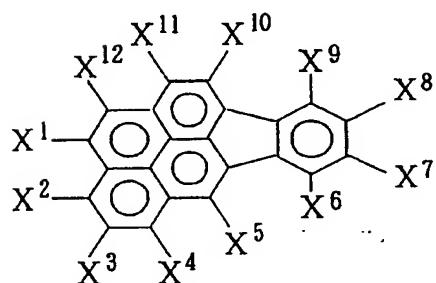
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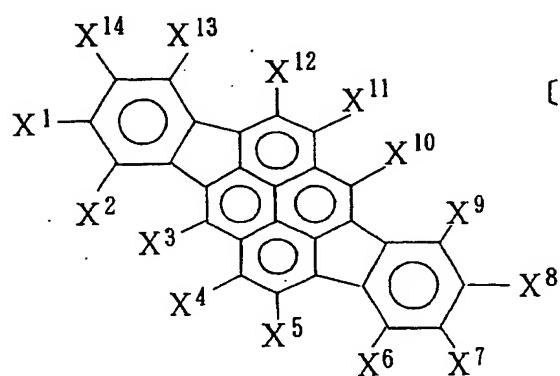
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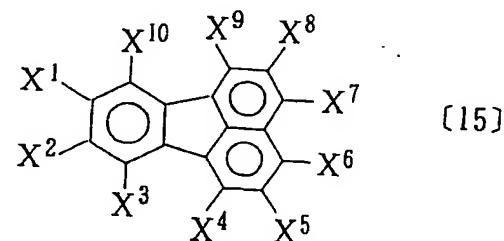
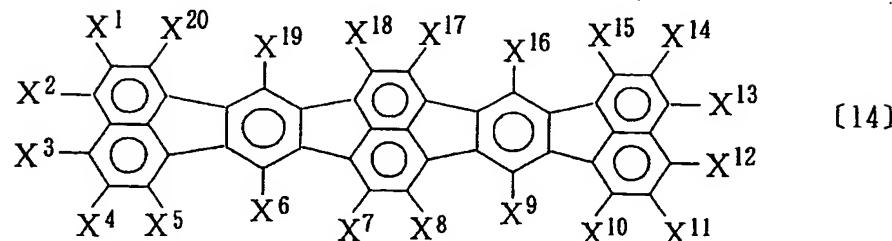
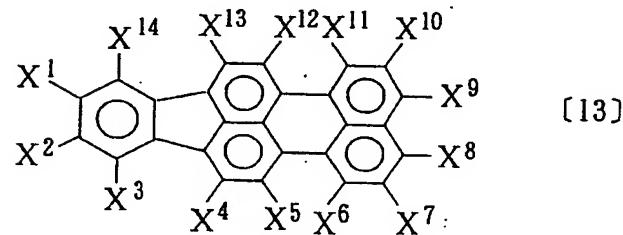
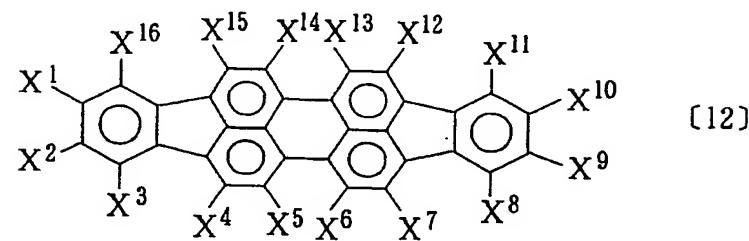
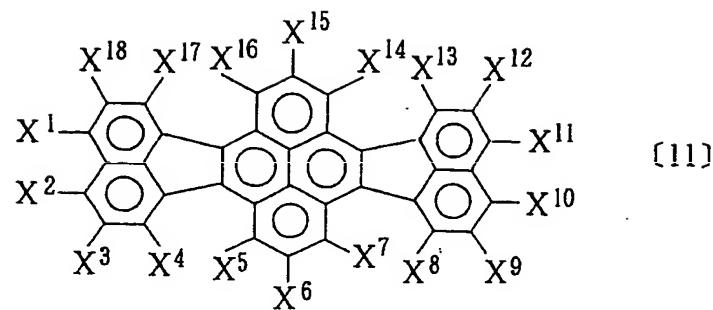
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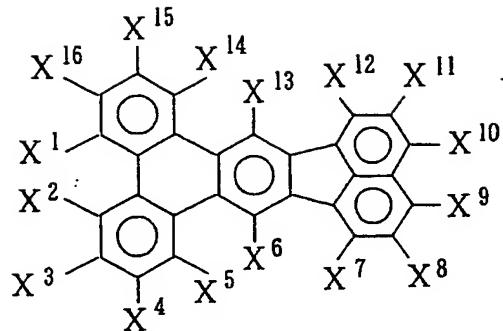


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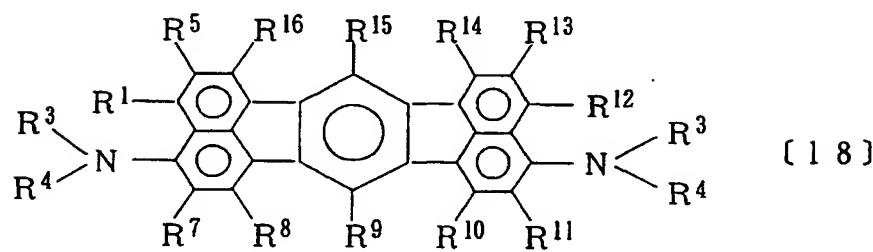
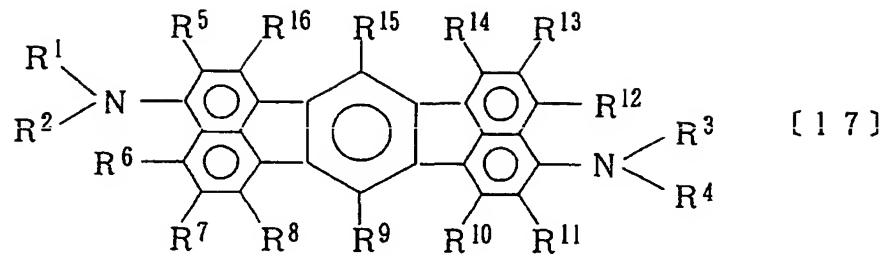




[16]

wherein  $X^1$  to  $X^{20}$  each independently represents hydrogen atom, a linear, branched or cyclic alkyl group having 1 to 20 carbon atoms, a linear, branched or cyclic alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon groups, a substituted or unsubstituted arylamino group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 30 carbon atoms, a substituted or unsubstituted arylalkylamino group having 7 to 30 carbon atoms or a substituted or unsubstituted alkenyl groups having 8 to 30 carbon atoms; a pair of adjacent groups represented by  $X^1$  to  $X^{20}$  and a pair of adjacent substituents to groups represented by  $X^1$  to  $X^{20}$  may form a cyclic structure in combination; when a pair of adjacent substituents are aryl groups, the pair of substituents may be a single group; and at least one of substituents represented by  $X^1$  to  $X^i$ ,  $i$  representing a number of 12 to 20, comprises an amine group or an alkenyl group;

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wherein R<sup>1</sup> to R<sup>4</sup> each independently represent an alkyl group having 1 to 20 carbon atoms or a substituted or unsubstituted aryl group having 6 to 30 carbon atoms; in one or both of a pair of groups represented by R<sup>1</sup> and R<sup>2</sup> and a pair of groups represented by R<sup>3</sup> and R<sup>4</sup>, the groups forming the pair may be bonded through -O- or -S-; R<sup>5</sup> to R<sup>16</sup> represents hydrogen atom, a linear, branched or cyclic alkyl group having 1 to 20 carbon atoms, a linear, branched or cyclic alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon groups, a substituted or unsubstituted arylamino group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 30 carbon atoms, a substituted or unsubstituted arylalkylamino group having 7 to 30 carbon atoms or a substituted or unsubstituted alkenyl groups having 8 to

30 carbon atoms; a pair of adjacent groups represented by R<sup>5</sup> to R<sup>16</sup> and a pair of adjacent substituents to groups represented by R<sup>5</sup> to R<sup>16</sup> may form a cyclic structure in combination; and at least one of substituents represented by R<sup>5</sup> to R<sup>16</sup> comprises an amine group or an alkenyl group.

The novel compound of the present invention is a compound represented by any of the above general formulae [1] to [18].

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the <sup>1</sup>H-NMR spectrum of an example of the novel compound of the present invention.

Figure 2 shows the <sup>1</sup>H-NMR spectrum of another example of the novel compound of the present invention.

Figure 3 shows the <sup>1</sup>H-NMR spectrum of still another example of the novel compound of the present invention.

#### THE MOST PREFERRED EMBODIMENT TO CARRY OUT THE INVENTION

The organic electroluminescence device of the present invention comprises an organic layer disposed between at least one pair of electrodes, wherein the organic layer comprises compounds having a fluoranthene skeleton structure substituted at least with an amine group or an alkenyl group.

This compound is a novel compound and is represented by any of the above general formulae [1] to [18].

In general formulae [1] to [16], X<sup>1</sup> to X<sup>20</sup> each independently represents hydrogen atom, a linear, branched or cyclic alkyl group having

1 to 20 carbon atoms, a linear, branched or cyclic alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon groups, a substituted or unsubstituted arylamino group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 30 carbon atoms, a substituted or unsubstituted arylalkylamino group having 7 to 30 carbon atoms or a substituted or unsubstituted alkenyl groups having 8 to 30 carbon atoms; a pair of adjacent groups represented by X<sup>1</sup> to X<sup>20</sup> and a pair of adjacent substituents to groups represented by X<sup>1</sup> to X<sup>20</sup> may form a cyclic structure in combination; when a pair of adjacent substituents are aryl groups, the pair of substituents may be a single group; and at least one of substituents represented by X<sup>1</sup> to X<sup>i</sup>, i representing a number of 12 to 20, comprises an amine group or an alkenyl group. That a pair of adjacent substituents may be a single group when the pair of adjacent substituents are aryl groups means that the adjacent bonds for the pair of substituents are bonded to the same single divalent aromatic ring group.

In general formulae [17] and [18], R<sup>1</sup> to R<sup>4</sup> each independently represent an alkyl group having 1 to 20 carbon atoms or a substituted or unsubstituted aryl group having 6 to 30 carbon atoms; in one or both of a pair of groups represented by R<sup>1</sup> and R<sup>2</sup> and a pair of groups represented by R<sup>3</sup> and R<sup>4</sup>, the groups forming the pair may be bonded through -O- or -S-; R<sup>5</sup> to R<sup>16</sup> represents hydrogen atom, a linear, branched or cyclic alkyl group having 1 to 20 carbon atoms, a linear, branched or cyclic alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aryloxy

group having 6 to 30 carbon groups, a substituted or unsubstituted arylamino group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 30 carbon atoms, a substituted or unsubstituted arylalkylamino group having 7 to 30 carbon atoms or a substituted or unsubstituted alkenyl groups having 8 to 30 carbon atoms; a pair of adjacent groups represented by R<sup>5</sup> to R<sup>16</sup> and a pair of adjacent substituents to groups represented by R<sup>5</sup> to R<sup>16</sup> may form a cyclic structure in combination; and at least one of substituents represented by R<sup>5</sup> to R<sup>16</sup> comprises an amine group or an alkenyl group.

Preferable compounds among the compounds represented by general formulae [1] to [18] are shown in the following.

It is preferable that the fluoranthene skeleton structure comprises at least 5 condensed rings and more preferably at least 6 condensed rings. By using the compounds having this structure, light having a longer wavelength such as yellowish to reddish light can be emitted.

It is preferable that the fluoranthene skeleton structure is substituted with an amino group. By using the compound having this structure, a light emitting material having a longer life can be obtained.

It is preferable that the amino group is a substituted or unsubstituted arylamino group and more preferably a substituted or unsubstituted diarylamino group. By using the compound having this structure, a device showing a smaller decrease in the light emission at increased concentrations of the compound and exhibiting a high efficiency can be obtained even when the above compound is added to the light emitting layer in a concentration as high as 2% or higher.

It is preferable that the above compound has a symmetric structure

having an axial symmetry or a symmetry with respect to plane. By using the compound having this structure, durability of the device is improved and the quantum efficiency of fluorescence is enhanced.

It is preferable that the above compound has at least ten six-membered rings or five-membered rings. The compound has a glass transition temperature of 100°C or higher due to this structure and heat stability of a layer composed of or comprising this compound is improved. It is preferable that the above compound has an aryl group, a cyclic alkyl group, an aryloxy group, an arylthio group or an arylalkyl group each having 4 or more carbon atoms. Since these groups exhibit steric hindrance and the decrease in the light emission at increased concentrations of the compound can be prevented.

It is preferable that, in general formulae [17] and [18], R<sup>15</sup> and R<sup>9</sup> each represent a group having a substituent. When the compound represented by general formula [17] or [18] has this structure, the compound has an improved stability against oxidation and reduction and the life of the device can be extended.

When the fluoranthene skeleton structure is substituted with two amino groups, two alkenyl groups or a combination of an amino group and an alkenyl group, the compound having this fluoranthene skeleton structure has isomers.

Examples of the isomers are described in the case where the fluoranthene skeleton structure is 7,14-diphenylacenaphtho[1,2-k]-fluoranthene.

Dibromo-substituted acenaphtho[1,2-k]fluoranthene has two isomers, i.e., 3,10-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthene

(isomer A) and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthene (isomer B).

The final product obtained from isomer A and isomer B as the intermediates contains an amino-substituted compound derived from isomer A and an amino-substituted compound derived from isomer B. When the final product is prepared, the relative amounts of isomer A and isomer B contained in the final product is different depending on the process of the preparation. (1) The dibromo-substituted compounds may be obtained from a solution portion of a reaction mixture in which the dibromo-substituted compounds are dissolved. (2) The dibromo-substituted compounds may also be obtained from precipitates formed by recrystallization from a solution which is obtained by dissolving the product obtained above from the solution portion of the reaction mixture. (3) The dibromo-substituted compounds may also be obtained from the solution left after the above recrystallization. By suitably selecting the process and the type of the solvent used for the treatment, the object compound containing various amounts of isomer A and isomer B and, specifically, having a ratio of the amount by mole of isomer A to the amount in mole of isomer B in the range of 10:90 to 90:10, can be obtained.

It is preferable that the error in the ratio of the amounts by mole of the isomers is: (i) isomer A : isomer B =  $x \pm 10 : y \pm 10$  ( $x+y=100$ ) and more preferably (ii) isomer A : isomer B =  $x \pm 5 : y \pm 5$  ( $x+y=100$ ). When the relation (i) is satisfied, the ratio of the amounts of the isomers will be described as approximately constant and, when the relation (ii) is satisfied, the ratio of the amounts of the isomers will be described as constant, hereinafter.

When the above compound of the present invention has isomers, a plurality of isomers can be comprised in the organic layer. It is preferable that the device is prepared under the condition that the ratio of the amounts of the isomers is kept approximately constant or constant. By preparing the device in this manner, the spectrum of the light emitted from the device can be kept the same. In other words, the color of the emitted light can be kept the same. Moreover, the color of the emitted light can be changed by changing the ratio of the amounts of the isomers. Naturally, the organic layer may comprise a single compound with exclusion of any other isomers.

When a compound contains isomers as described above, one of the isomers can emit light having a longer wavelength than that of light emitted from other isomers. Therefore, light having a longer wavelength such red light can be emitted when the ratio of the amount by mole of the isomer which can emit light having a longer wavelength to the amount by mole of the isomer which can emit light having a shorter wavelength is preferably in the range of 90:10 to 60:40 and more preferably in the range of 99:1 to 70:30.

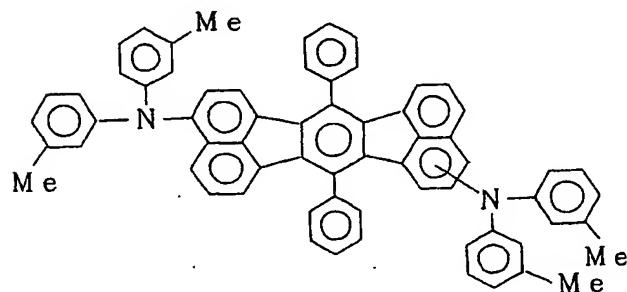
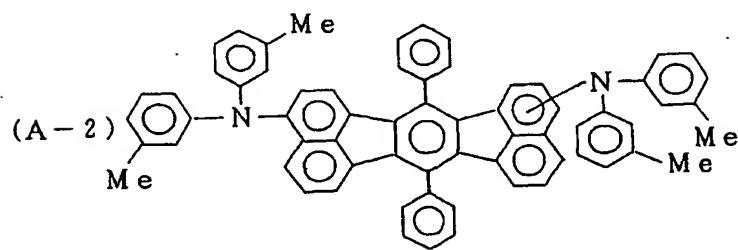
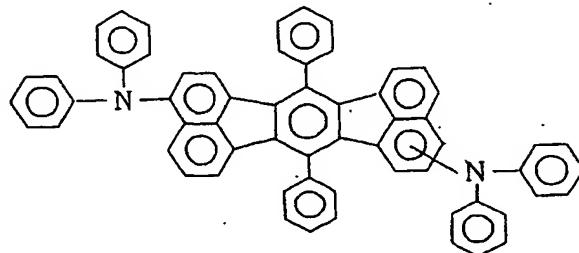
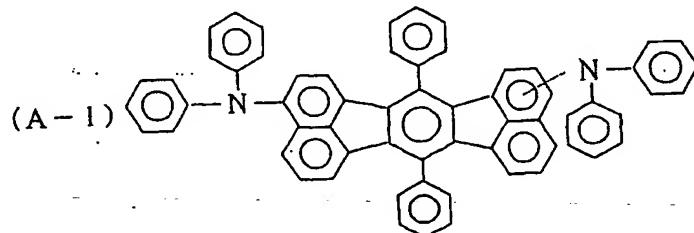
Taking advantage of the difference in the chemical shift in  $^1\text{H-NMR}$  between the isomers, the ratio of the amounts of the isomers can be calculated from the ratio of the areas of peak signals assigned to each isomer.

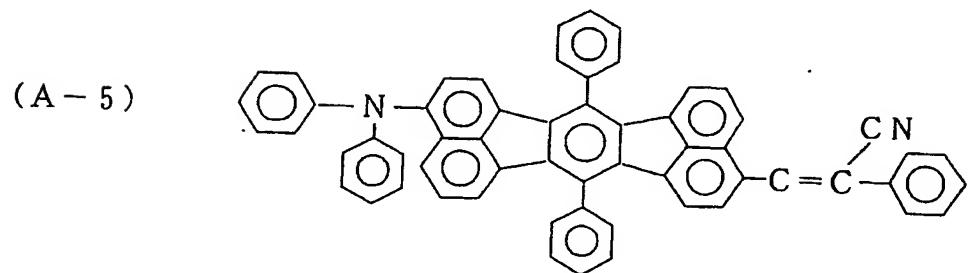
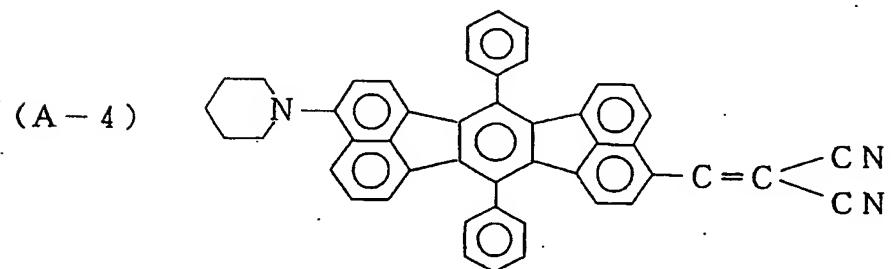
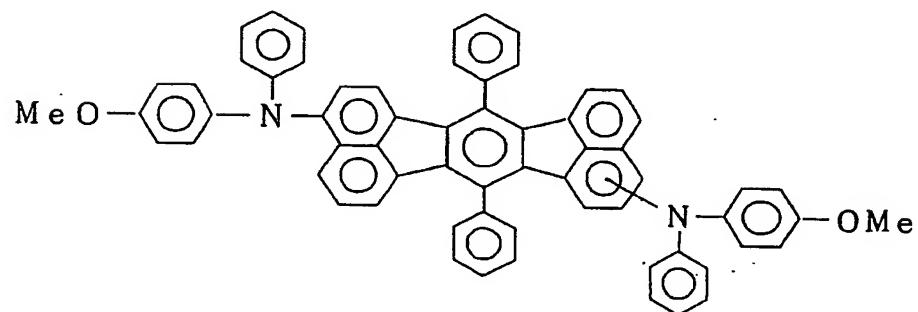
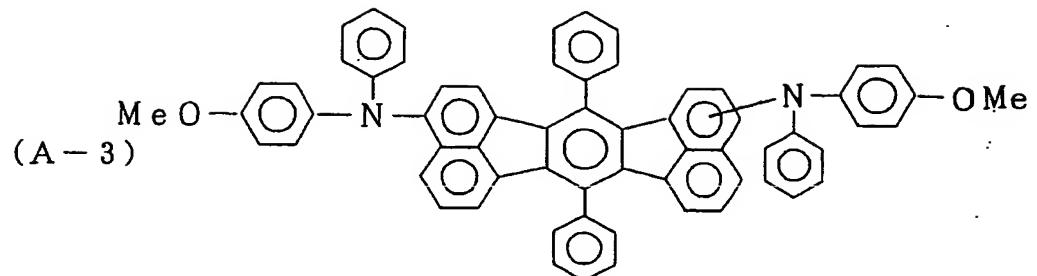
It is preferable that the organic layer is at least one of a hole transportation layer and a light emitting layer.

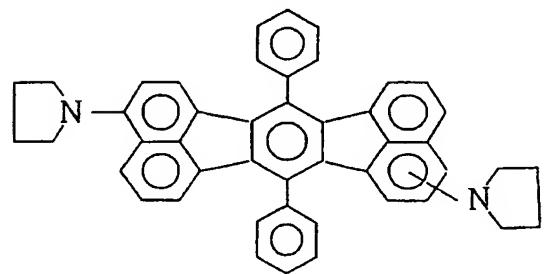
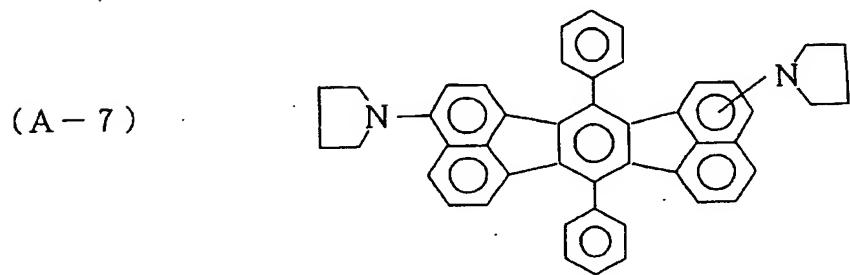
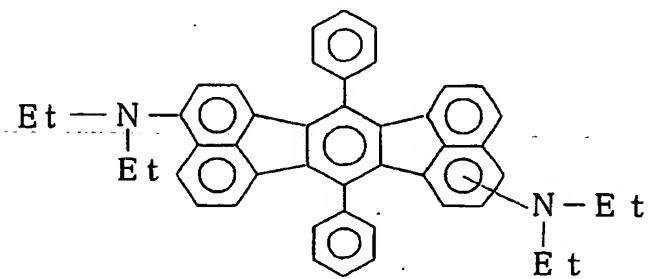
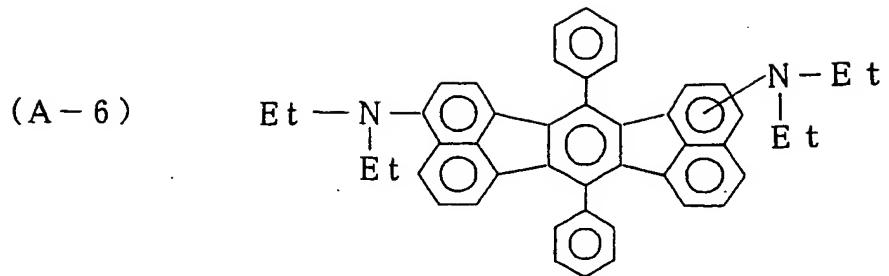
A layer of an inorganic compound may be disposed between the organic layer and the electrode.

The organic EL device of the present invention emits reddish light.

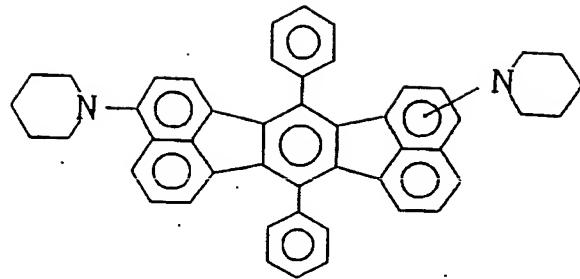
Examples of the compounds represented by general formulae [1] to [18] of the present invention include (A-1) to (A-18) and (B-1) to (B-17) which are shown in the following. However, the present invention is not limited to these compounds shown as the examples. In the formulae shown in the following, Me means methyl group and Et means ethyl group.



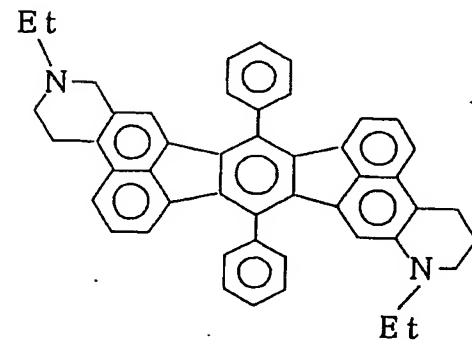




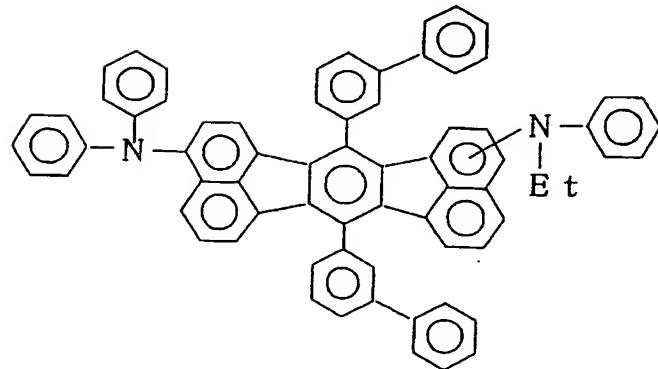
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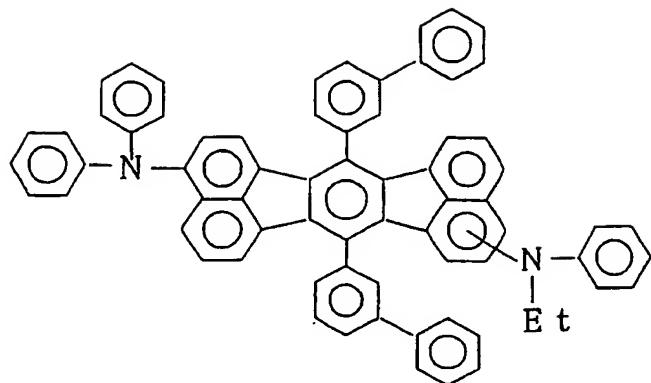


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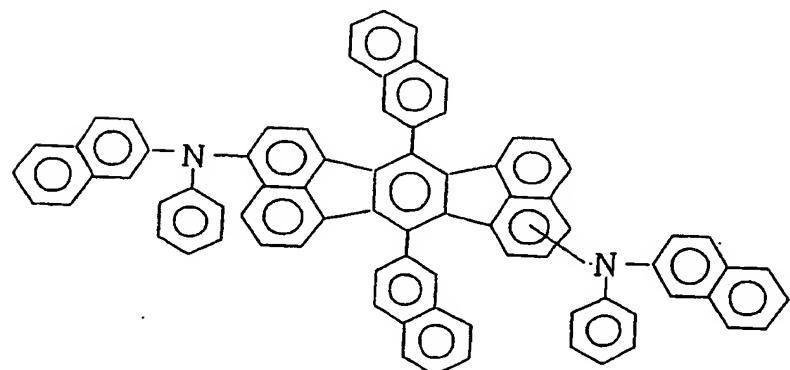
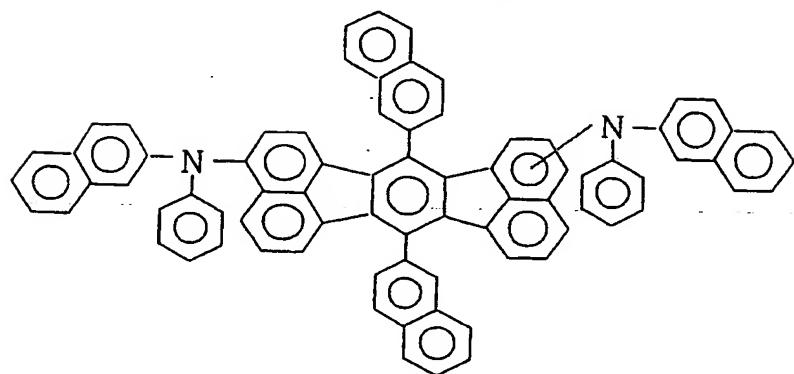


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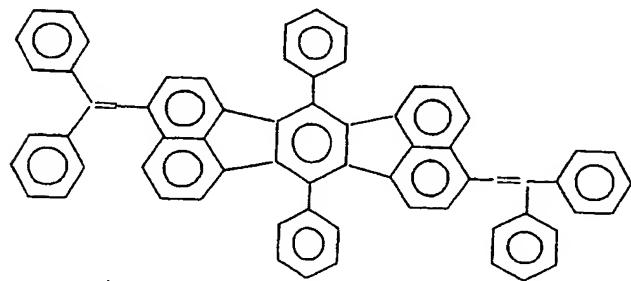




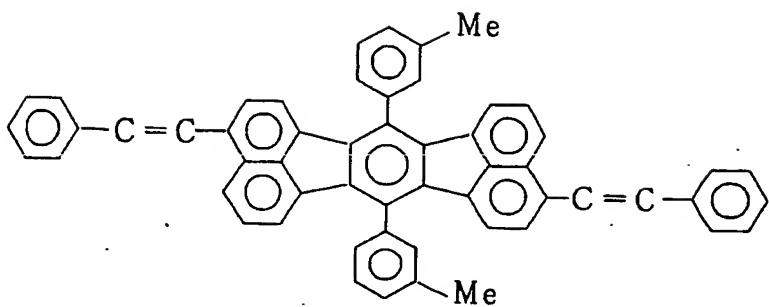
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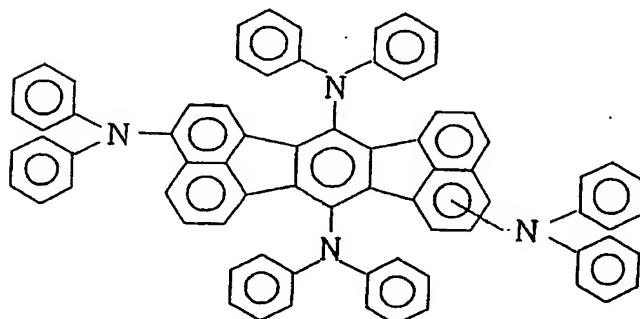
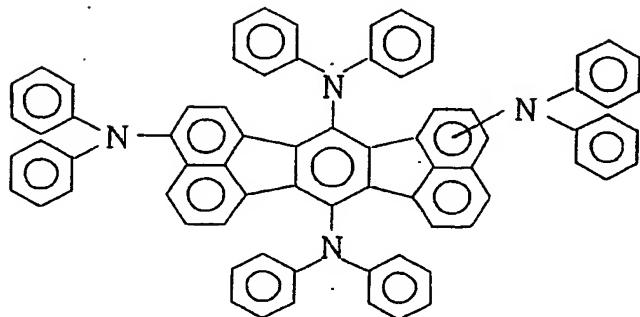
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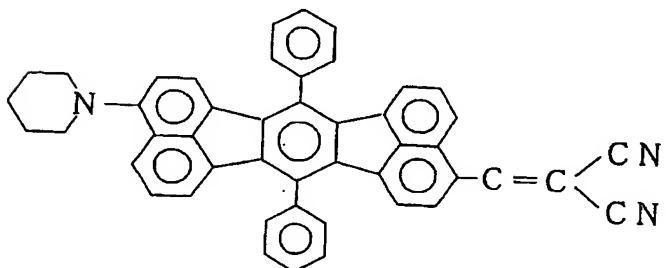
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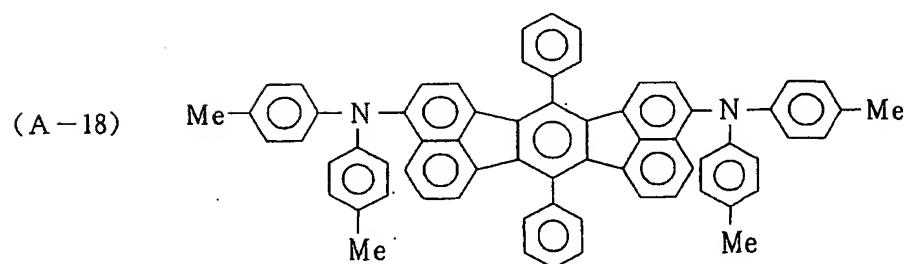
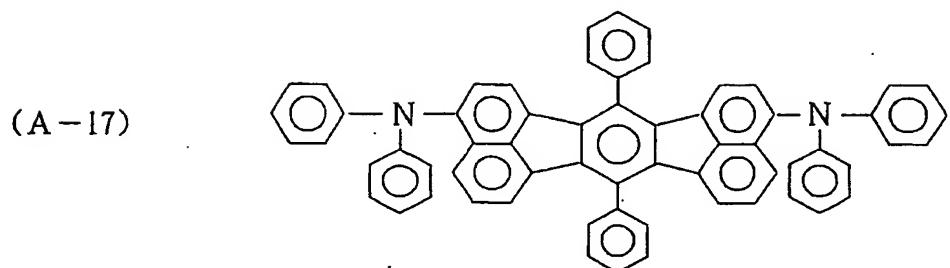
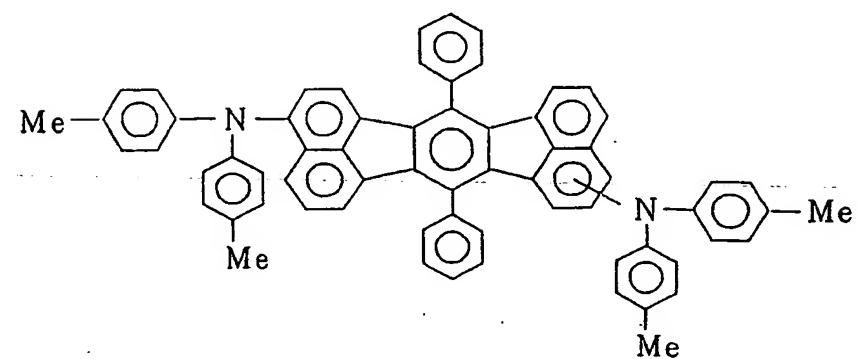
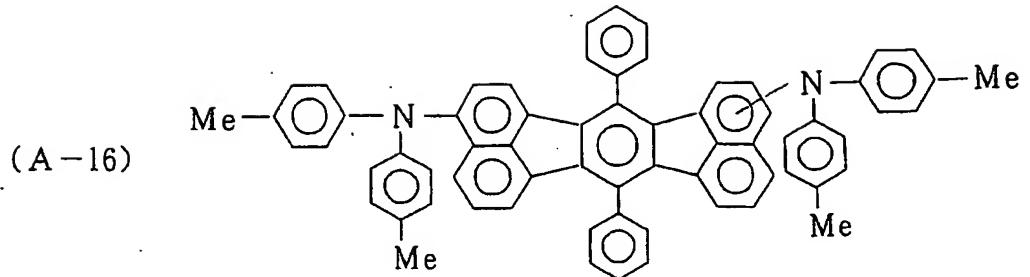


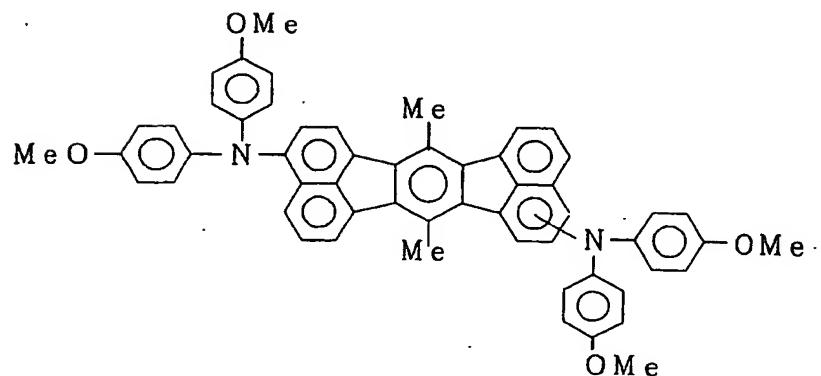
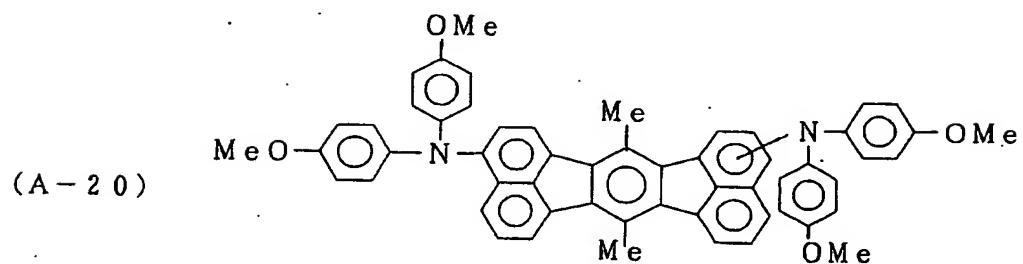
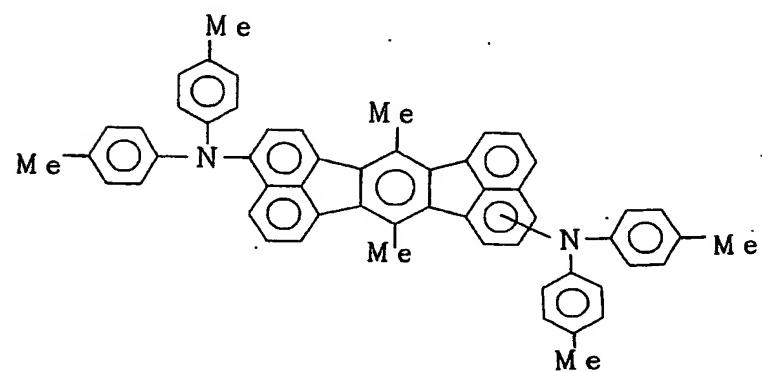
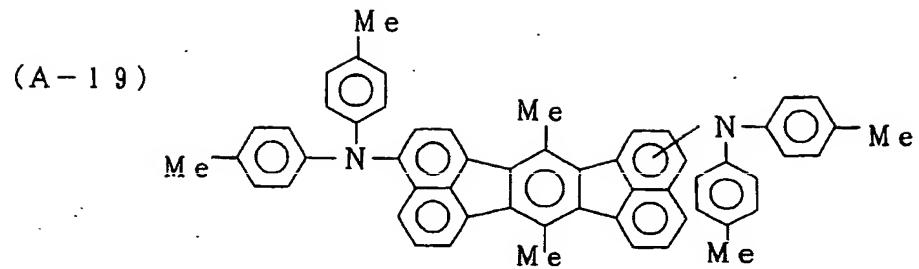
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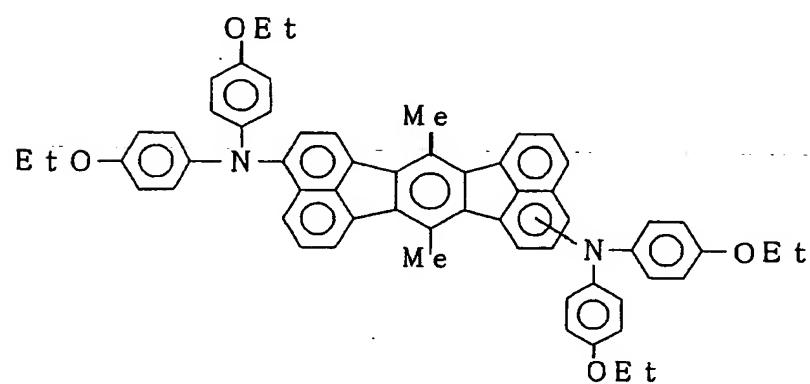
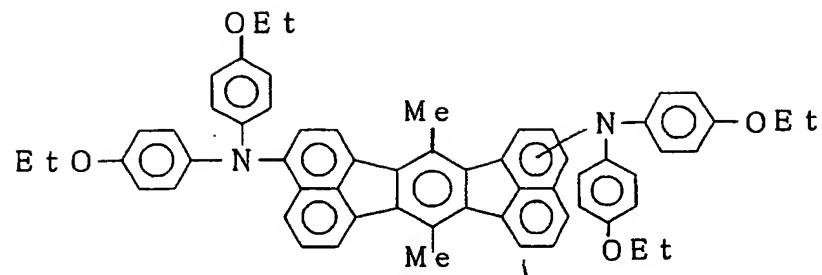
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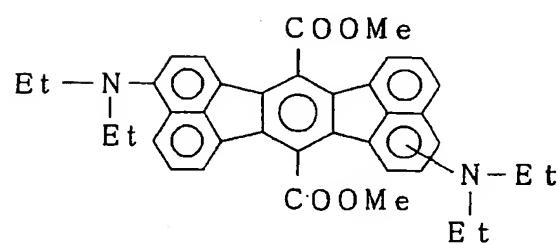
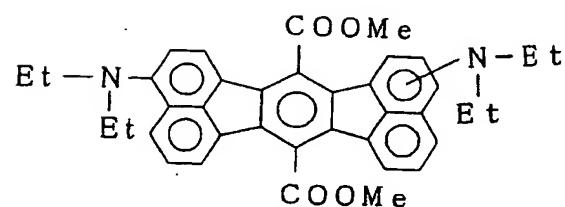




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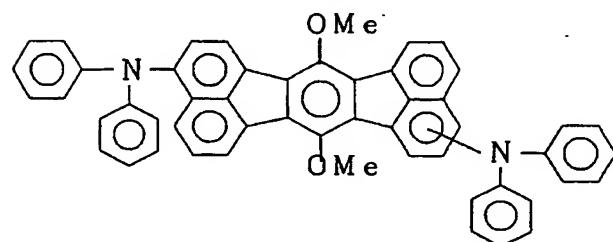
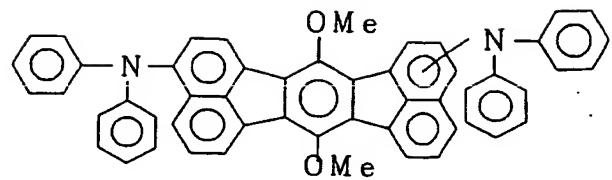


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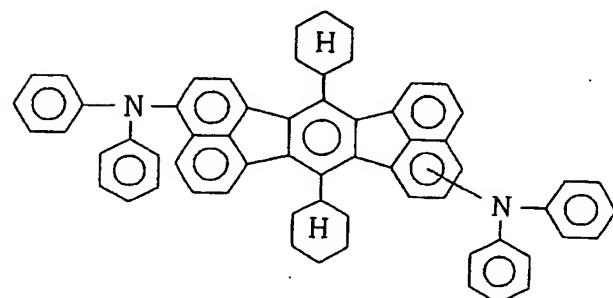
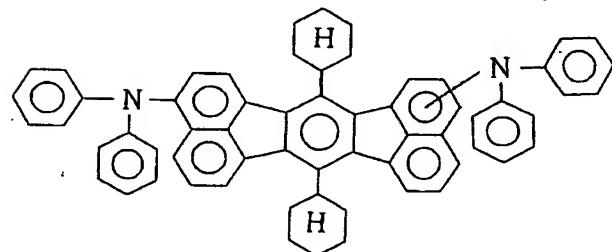


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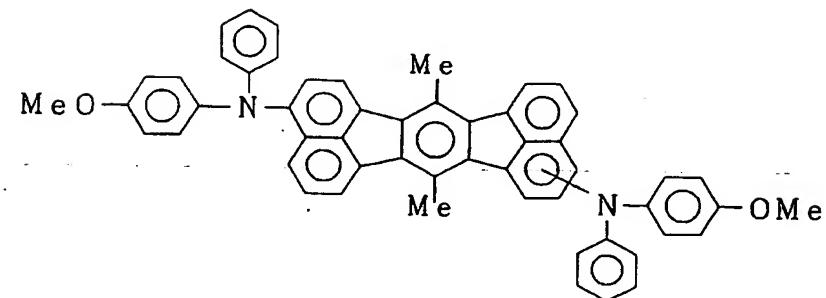
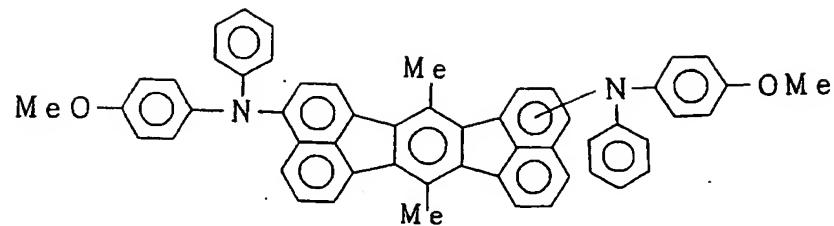
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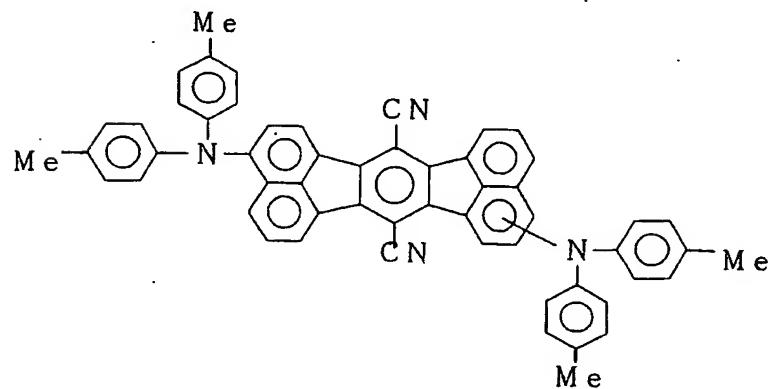
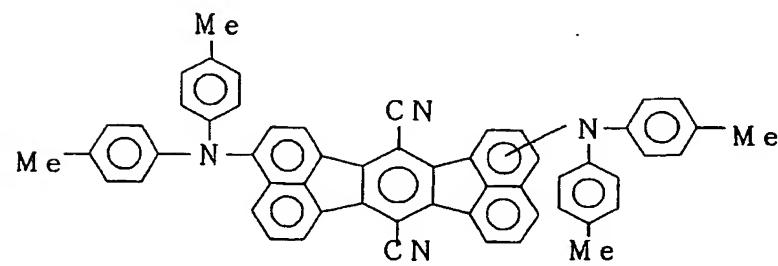
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(A - 2 5)

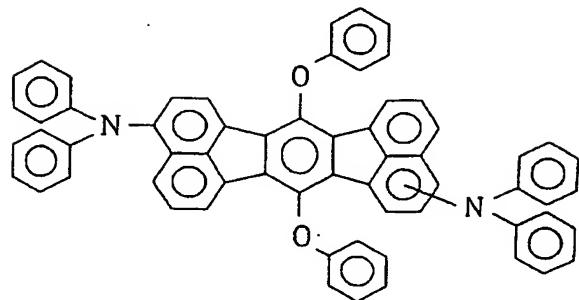
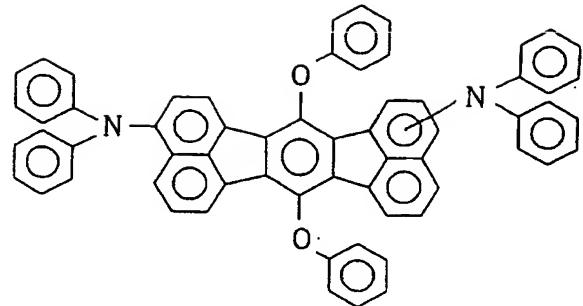


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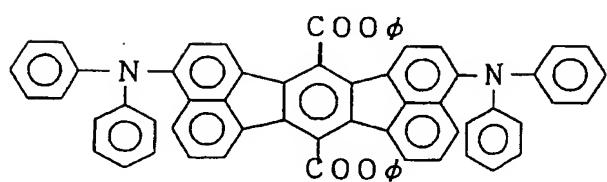


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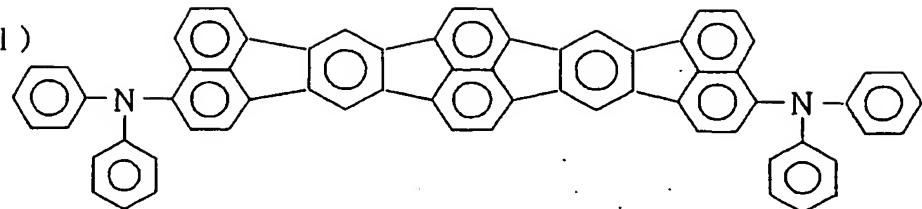


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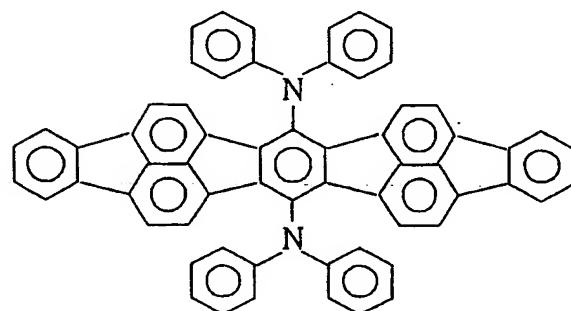


( $\phi$  is phenyl group)

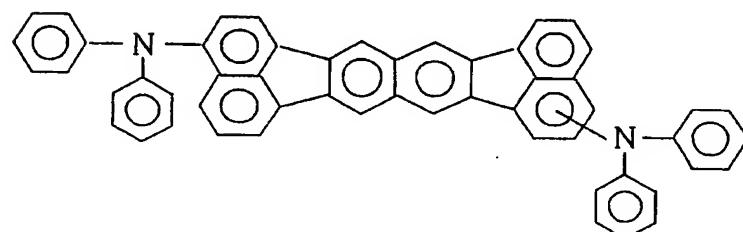
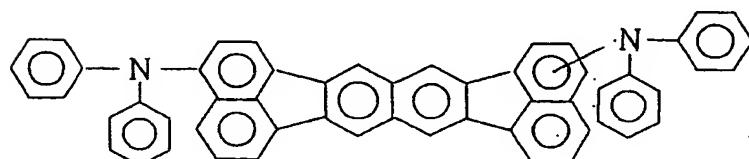
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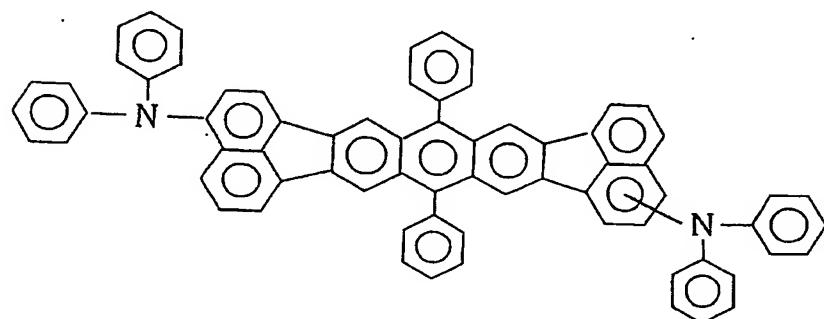
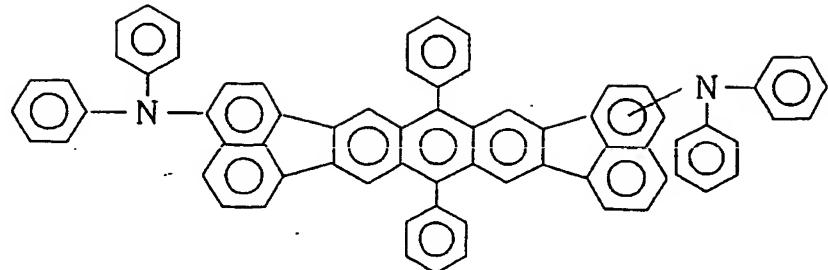
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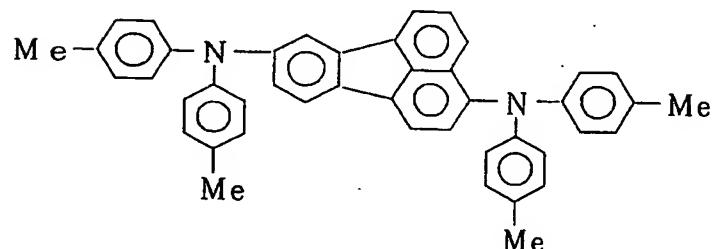
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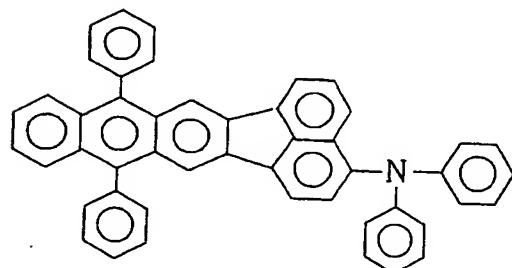
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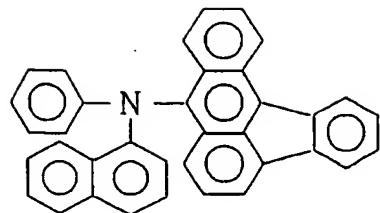
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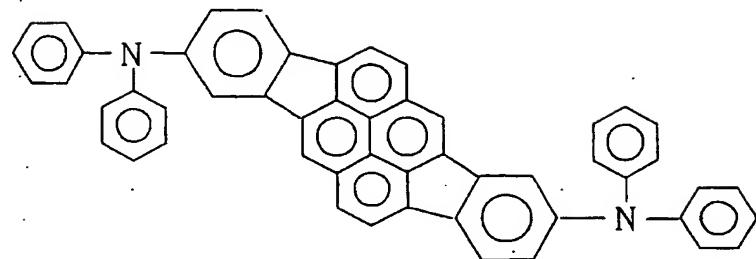
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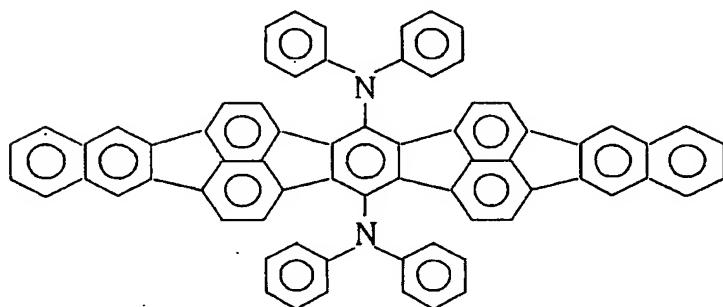
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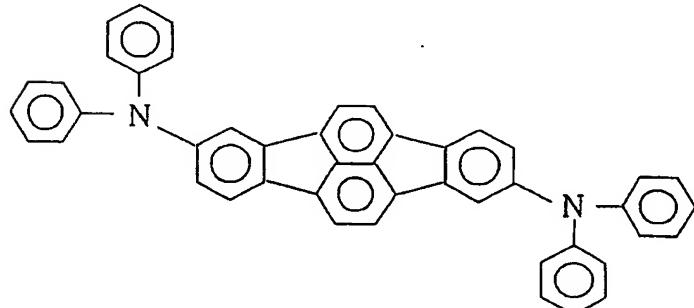
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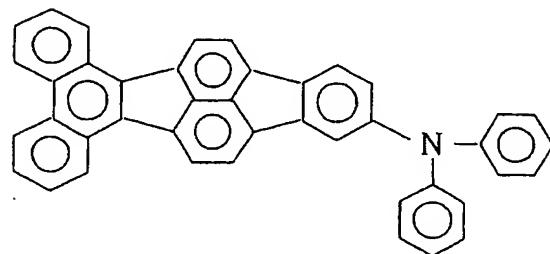
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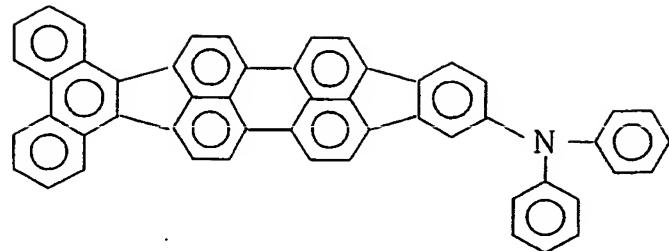
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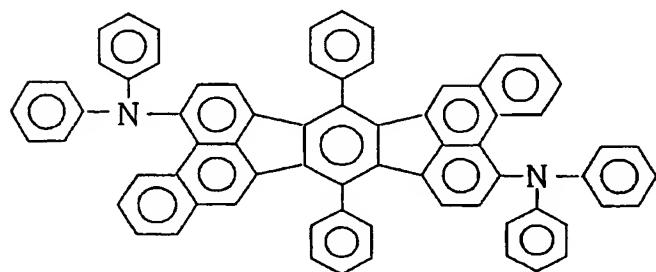
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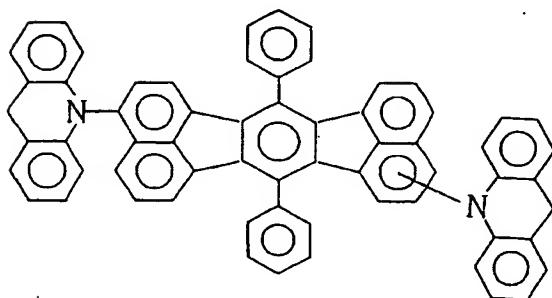
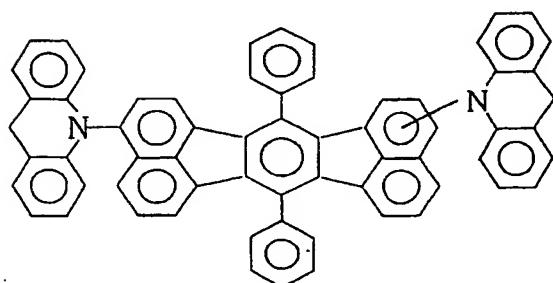
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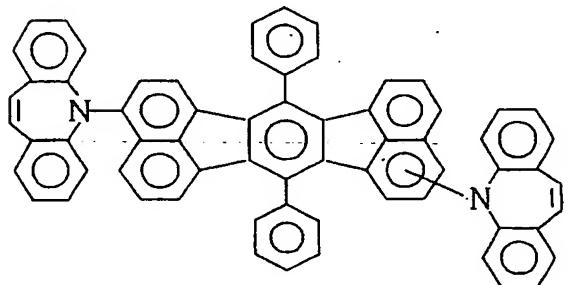
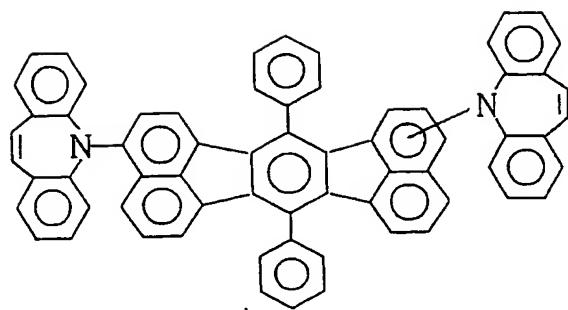
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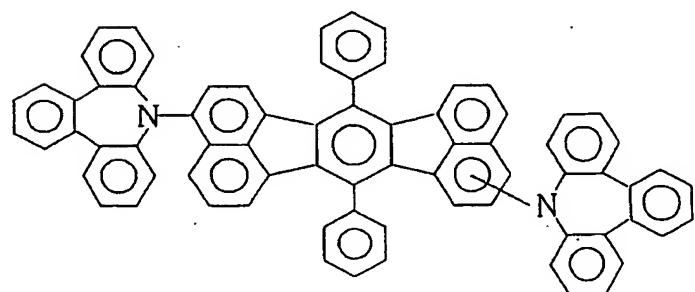
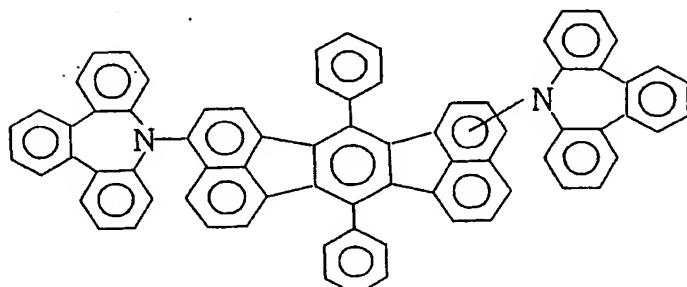
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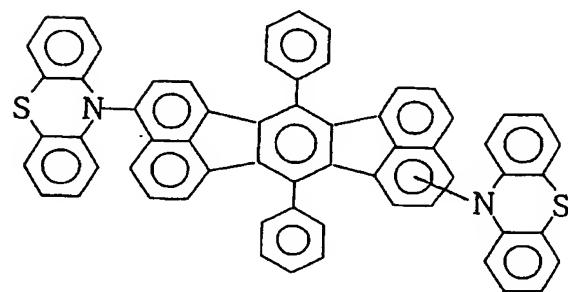
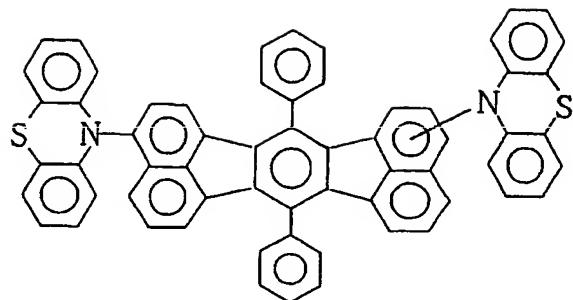
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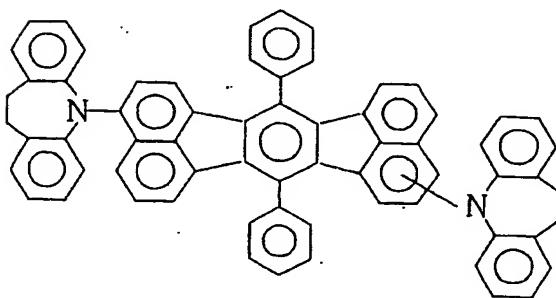
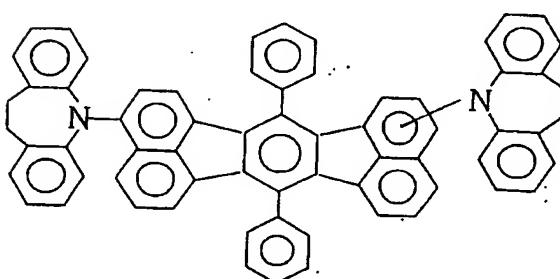
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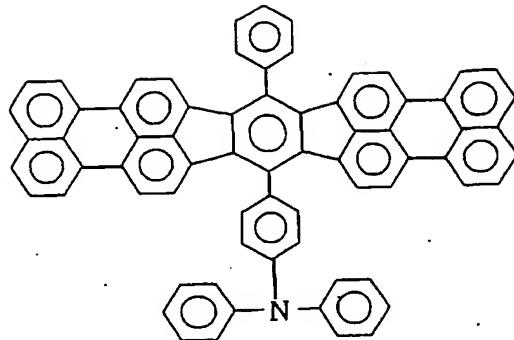
(B-17)



(B-18)



(B - 19)



Since the compound used for the organic EL device of the present invention has the fluoranthene skeleton structure substituted with an amine group or an alkenyl group, the compound exhibits a high yield of fluorescence and emits reddish or yellowish light. Therefore, the organic EL device using this compound emits reddish to yellowish light, exhibits a high efficiency of light emission and has a long life.

The organic EL device of the present invention is a device in which one or a plurality of organic thin films are disposed between an anode and a cathode. When the device has a single organic layer, a light emitting layer is disposed between an anode and a cathode. The light emitting layer contains a light emitting material and may also contain a hole injecting material to transport holes injected at the anode to the light emitting material or an electron injecting material to transport electrons injected at the cathode to the light emitting material. It is preferable that the light emitting layer is formed with a light emitting material having a very high quantum efficiency of fluorescence emission and excellent ability to transfer holes and electrons and a uniform thin film is formed. The organic EL device having a multi-layer structure has a laminate structure such as: (an anode / a hole injecting layer / a light emitting layer / a

cathode), (an anode / a light emitting layer / an electron injecting layer / a cathode) and (an anode / a hole injecting layer / a light emitting layer / an electron injecting layer / a cathode).

In the light emitting layer, where necessary, conventional light emitting materials, doping materials, hole injecting materials and electron injecting materials may be used in addition to the compound represented by any of general formulae [1] to [18] of the present invention. It is preferable that these compounds are added to any of the light emitting layer, the electron injecting layer, the hole transporting layer or the hole injecting layer in a concentration of 1 to 70% by weight and more preferably in a concentration of 1 to 20% by weight. In particular, it is preferable that the compound of the present invention is used as the doping material.

Deterioration in the luminance and the life caused by quenching can be prevented by the multi-layer structure of the organic EL. Where necessary, light emitting materials, other doping materials, hole injecting materials and electron injecting materials may be used in combination. By using other doping materials, the luminance and the efficiency of light emission can be improved and red light and white light can be emitted. The hole injecting layer, the light emitting layer and the electron injecting layer may each have a multi-layer structure having two or more layers. When the hole injecting layer has a multi-layer structure, the layer into which holes are injected from the electrode is referred to as the hole injecting layer and the layer which receives holes from the hole injecting layer and transports holes from the hole injecting layer to the light emitting layer is referred to as the hole transporting layer. When the

electron injecting layer has a multi-layer structure, the layer into which electrons are injected from the electrode is referred to as the electron injecting layer and the layer which receives electrons from the electron injecting layer and transports electrons from the electron injecting layer to the light emitting layer is referred to as the electron transporting layer. These layers are each selected and used in accordance with factors such as the energy level, heat resistance and adhesion with the organic layers or the metal electrodes of the material.

Examples of the material which can be used in the organic layer as the light emitting material or the host material in combination with the compound represented by any of general formulae [1] to [18] include anthracene, naphthalene, phenanthrene, pyrene, tetracene, coronene, chrysene, fluoresceine, perylene, phthaloperylene, naphthaloperylene, perynone, phthaloperynone, naphthaloperynone, diphenylbutadiene, tetraphenylbutadiene, coumarine, oxadiazole, aldazine, bisbenzoxazoline, bisstyryl, pyrazine, cyclopentadiene, metal complexes of quinoline, metal complexes of aminoquinoline, metal complexes of benzoquinoline, imines, diphenylethylene, vinylanthracene, diaminocarbazole, pyrane, thiopyrane, polymethine, merocyanine, chelates of oxinoid compounds with imidazoles, quinacridone, rubrene, stilbene derivatives and fluorescent pigments. However, the above material is not limited to the compounds described above as the examples.

As the hole injecting material, a compound which has the ability to transfer holes, exhibits an excellent effect of hole injection from the anode and an excellent effect of hole injection to the light emitting layer or the light emitting material, prevents transfer of excited components formed in

the light emitting layer into the electron injecting layer or the electron injecting material and has excellent ability to form a thin film is preferable. Examples of the above compound include phthalocyanine derivatives, naphthalocyanine derivatives, porphyrin derivatives, oxazole, oxadiazole, triazole, imidazole, imidazolone, imidazolethione, pyrazoline, pyrazolone, tetrahydroimidazole, oxazole, oxadiazole, hydrazone, acylhydrazone, polyarylalkanes, stilbene, butadiene, triphenylamines of the benzidine-type, triphenylamines of the styrylamine type, triphenylamines of the diamine type, derivatives of these compounds and macromolecular compounds such as polyvinylcarbazole, polysilane and conductive macromolecules. However, the above compound is not limited to the compounds described above as the examples.

Among the hole injection materials which can be used in the organic EL device of the present invention, aromatic tertiary amine derivatives and phthalocyanine derivatives are more effective.

Examples of the aromatic tertiary amine derivative include triphenylamine, tritylamine, tolyldiphenylamine, N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N,N',N'-(4-methylphenyl)-1,1'-phenyl-4,4'-diamine, N,N,N',N'-(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N'-diphenyl-N,N'-dinaphthyl-1,1'-biphenyl-4,4'-diamine, N,N'-(methylphenyl)-N,N'-(4-n-butylphenyl)phenanthrene-9,10-diamine, N,N-bis(4-di-4-tolylaminophenyl)-4-phenylcyclohexane and oligomers and polymers having a skeleton structure of these aromatic tertiary amines. However, the aromatic tertiary amine derivative is not limited to the compounds described above as the examples.

Examples of the phthalocyanine (Pc) derivative include H<sub>2</sub>Pc, CuPc,

CoPc, NiPc, ZnPc, PdPc, FePc, MnPc, ClAlPc, ClGaPc, ClInPc, ClSnPc, Cl<sub>2</sub>SiPc, (HO)AlPc, (HO)GaPc, VOPc, TiOPc, MoOPc, GaPc-O-GaPc and corresponding derivatives of naphthalocyanine. However, the derivatives of phthalocyanine and naphthalocyanine are not limited to the compounds described above as the examples.

As the electron injecting material, a compound which has the ability to transport electrons, exhibits an excellent effect of electron injection from the cathode and an excellent effect of electron injection to the light emitting layer or the light emitting material, prevents transfer of excited components formed in the light emitting layer into the hole injecting layer and has excellent ability to form a thin film is preferable. Examples of the above compound include fluorenone, anthraquinodimethane, diphenoquinone, thiopyrane dioxide, oxazole, oxadiazole, triazole, imidazole, perylenetetracarboxylic acid, fluorenylidenemethane, anthraquinodimethane, anthrone and derivatives of these compounds. However, the above compound is not limited to the compounds described above as the examples. The charge injecting property can be improved by adding an electron accepting material to the hole injecting material or by adding an electron donating material to the electron injecting material.

In the organic EL device of the present invention, more effective electron injecting materials are metal complex compounds and five-membered derivatives containing nitrogen.

Examples of the metal complex compound include 8-hydroxy-quinolinatolithium, bis(8-hydroxyquinolinato)zinc, bis(8-hydroxy-quinolinato)copper, bis(8-hydroxyquinolinato)manganese, tris(8-hydroxy-quinolinato)aluminum, tris(2-methyl-8-hydroxyquinolinato)aluminum,

tris(8-hydroxyquinilinato)gallium, bis(10-hydroxybenzo[h]quinolinato)-beryllium, bis(10-hydroxybenzo[h]quinolinato)zinc, bis(2-methyl-8-quinolinato)chlorogallium, bis(2-methyl-8-quinolinato)(o-cresolato)gallium, bis(2-methyl-8-quinolinato)(1-naphtholato)aluminum and bis(2-methyl-8-quinolinato)(2-naphtholato)gallium. However, the metal complex compound is not limited to the compounds described above as the examples.

Preferable examples of the five-membered derivative containing nitrogen include derivatives of oxazoles, thiazoles, thiadiazoles and triazoles. Specific examples include 2,5-bis(1-phenyl)-1,3,4-oxazole, dimethylPOPOP, 2,5-bis(1-phenyl)-1,3,4-thiazole, 2,5-bis(1-phenyl)-1,3,4-oxadiazole, 2-(4'-tert-butylphenyl)-5-(4"-biphenyl)-1,3,4-oxadiazole, 2,5-bis(1-naphthyl)-1,3,4-oxadiazole, 1,4-bis[2-(5-phenyloxadiazolyl)]benzene, 1,4-bis[2-(5-phenyloxadiazolyl)-4-tert-butylbenzene], 2-(4'-tert-butylphenyl)-5-(4"-biphenyl)-1,3,4-thiadiazole, 2,5-bis(1-naphthyl)-1,3,4-thiadiazole, 1,4-bis[2-(5-phenylthiadiazolyl)]benzene, 2-(4'tert-butylphenyl)-5-(4"-biphenyl)-1,3,4-triazole, 2,5-bis(1-naphthyl)-1,3,4-triazole and 1,4-bis[2-(5-phenyltriazolyl)]benzene. However, the five-membered derivative containing nitrogen is not limited to the compounds described above as the examples.

In the organic EL device of the present invention, the organic layer may contain at least one of light emitting materials, doping materials, hole injecting materials and electron injecting materials in the same layer in addition to the compound represented by any of general formulae [1] to [18]. In order to improve stability of the organic EL device of the present invention with respect to the temperature, the humidity and the

atmosphere, a protecting layer may be formed on the surface of the device or the entire device may be protected with silicon oil or a resin.

As the conductive material used for the anode of the organic EL device, a material having a work function of 4 eV or greater is suitable. Examples of such a material include carbon, aluminum, vanadium, iron, cobalt, nickel, tungsten, silver, gold, platinum, palladium, alloys of these metals, metal oxides used for ITO substrates and NESA substrates such as tin oxide and indium oxide and organic conductive resins such as polythiophene and polypyrrol. As the conductive material used for the cathode, a material having a work function smaller than 4 eV is suitable. Examples of such a material include magnesium, calcium, tin, lead, titanium, yttrium, lithium, ruthenium, manganese, aluminum and alloys of these metals. However, the materials used for the anode and the cathode are not limited to the materials described above as the examples. Typical examples of the alloy include alloys of magnesium and silver, alloys of magnesium and indium and alloys of lithium and aluminum. However, the alloy is not limited to these alloys described as the examples. The composition of the alloy is controlled by the temperature of the source of vapor deposition, the atmosphere and the degree of vacuum and can be adjusted suitably. The anode and the cathode may have a multi-layer structure having two or more layers, where necessary.

In the organic EL device of the present invention, it is preferable that a layer of a chalcogenide, a metal halide or a metal oxide (this layer may occasionally be referred to as a surface layer) is disposed on the surface of at least one of the pair of electrodes prepared as described above. Specifically, it is preferable that a layer of a chalcogenide (including an

oxide) of a metal such as silicon and aluminum is disposed on the surface of the anode at the side of the layer of the light emitting medium and a layer of a metal halide or a metal oxide is disposed on the surface of the cathode at the side of the layer of the light emitting medium. Due to the above layers, stability in driving can be improved.

Preferable examples of the chalcogenide include  $\text{SiO}_x$  ( $1 \leq x \leq 2$ ),  $\text{AlO}_x$  ( $1 \leq x \leq 1.5$ ),  $\text{SiON}$  and  $\text{SiAlON}$ . Preferable examples of the metal halide include  $\text{LiF}$ ,  $\text{MgF}_2$ ,  $\text{CaF}_2$  and fluorides of rare earth metals. Preferable examples of the metal oxide include  $\text{Cs}_2\text{O}$ ,  $\text{Li}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{SrO}$ ,  $\text{BaO}$  and  $\text{CaO}$ .

In the organic EL device of the present invention, it is preferable that a mixed region of an electron transmitting compound and a reducing dopant or a mixed region of a hole transmitting compound and an oxidizing dopant is disposed on the surface of at least one of the pair of electrodes prepared as described above. Due to the mixed region disposed on the surface of the pair of electrodes, the electron transmitting compound is reduced to form an anion and injection and transportation of electrons from the mixed region into the light emitting medium can be facilitated. The hole transmitting compound is oxidized to form a cation and injection and transportation of holes from the mixed region into the light emitting medium is facilitated. Preferable examples of the oxidizing dopant include various types of Lewis acid and acceptor compounds. Preferable examples of the reducing dopant include alkali metals, compounds of alkali metals, alkaline earth metals, rare earth metals and compounds of these metals.

In the organic EL device, to achieve efficient light emission, it is

preferable that at least one face of the device is sufficiently transparent in the wave length region of the emitted light. It is preferable that the substrate is also transparent. The transparent electrode is disposed in accordance with vapor deposition or sputtering using the above conductive material in a manner such that the prescribed transparency is surely obtained. It is preferable that the electrode disposed on the light emitting face has a transmittance of light of 10% or greater. The substrate is not particularly limited as long as the substrate has sufficient mechanical strength and strength at high temperatures and is transparent. Glass substrates or transparent films of resins may be used. Example of the transparent films of resins include films of polyethylene, ethylene-vinyl acetate copolymers, ethylene-vinyl alcohol copolymers, polypropylene, polystyrene, polymethyl methacrylate, polyvinyl chloride, polyvinyl alcohol, polyvinyl butyral, nylon, polyether ether ketones, polysulfones, polyether sulfones, tetrafluoroethylene-perfluoroalkyl vinyl ether copolymers, polyvinyl fluoride, tetrafluoroethylene-ethylene copolymers, tetrafluoroethylene-hexafluoropropylene copolymers, polychlorotrifluoro-ethylene, polyvinylidene fluoride, polyesters, polycarbonates, polyurethanes, polyimides, polyether imides, polyimides and polypropylene.

Each layer of the organic EL device of the present invention can be formed suitably in accordance with a dry process of film formation such as vacuum vapor deposition, sputtering, plasma plating and ion plating or a wet process of film formation such as spin coating, dipping and flow coating. The thickness of the film is not particularly limited. However, it is necessary that the thickness be set at a suitable value. When the thickness is greater than the suitable value, a high voltage must be applied

to obtain a prescribed output of light and the efficiency decreases. When the thickness is smaller than the suitable value, pin holes are formed and a sufficient luminance cannot be obtained even when the electric field is applied. In general, the suitable range of the thickness is 5 nm to 10  $\mu$ m. A thickness in the range of 10 nm to 0.2  $\mu$ m is preferable.

When the device is produced in accordance with a wet process, materials forming each layer are dissolved or dispersed in a suitable solvent such as ethanol, chloroform, tetrahydrofuran and dioxane and a film is formed from the solution or the suspension. The solvent is not particularly limited. In any organic thin layer, suitable resins and additives may be used to improve the property to form a film and to prevent formation of pin holes. Examples of the resin which can be used include insulating resins such as polystyrene, polycarbonates, polyarylates, polyesters, polyamides, polyurethanes, polysulfones, polymethyl methacrylate, polymethyl acrylate and cellulose, copolymers derived from these resins, photoconductive resins such as poly-N-vinylcarbazole and polysilane and conductive resins such as polythiophene and polypyrrol. Examples of the additive include antioxidants, ultraviolet light absorbents and plasticizers.

As described above, when the compound of the present invention is used for the organic layer of the organic EL device, the organic EL device exhibiting an excellent purity of color and a high efficiency of light emission, having a long life and emitting red light can be obtained.

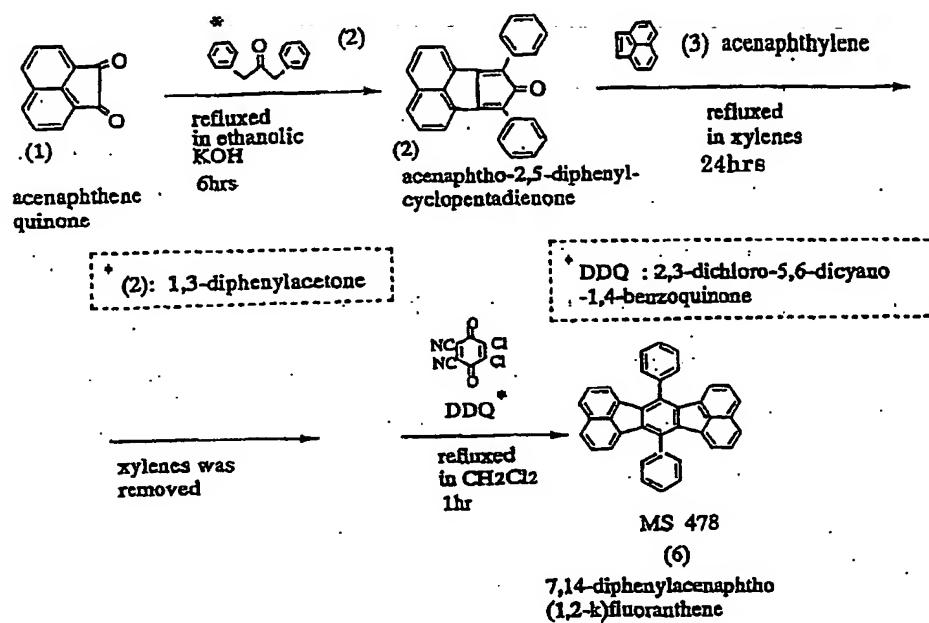
The organic EL device of the present invention can be used for a planar light emitting member such as a flat panel display of wall televisions, a back light for copiers, printers and liquid crystal displays, a

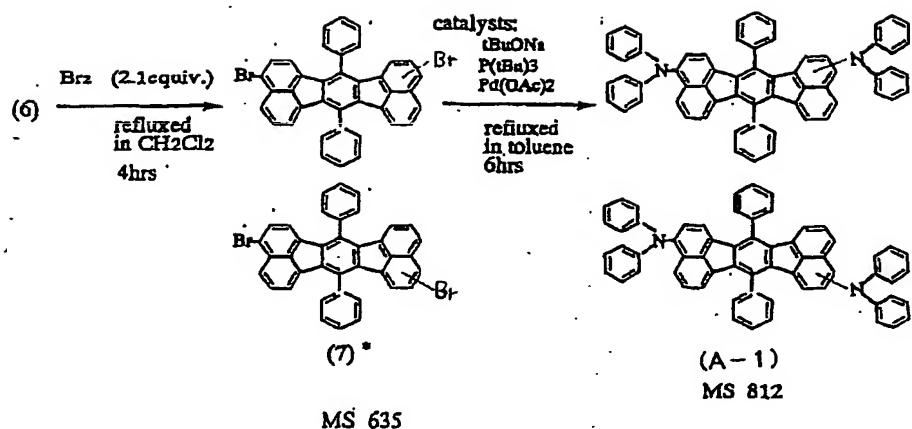
light source of instruments, display panels and a marker light.

The present invention will be described more specifically with reference to Synthesis Examples and Examples in the following.

#### Synthesis Example 1 (Compound A-1)

3,10- and 3,11-Bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]-fluoranthene was synthesized via the reaction route shown in the following:





\* (1) → (7)

cf. Jeff D. Debad, Allen J. Bard J. Am. Chem. Soc. vol.120 2476 (1998).

**(A) Synthesis of 3,10- and 3,11-dibromo-7,14-diphenyl-acenaphtho[1,2-k]fluoranthenes**

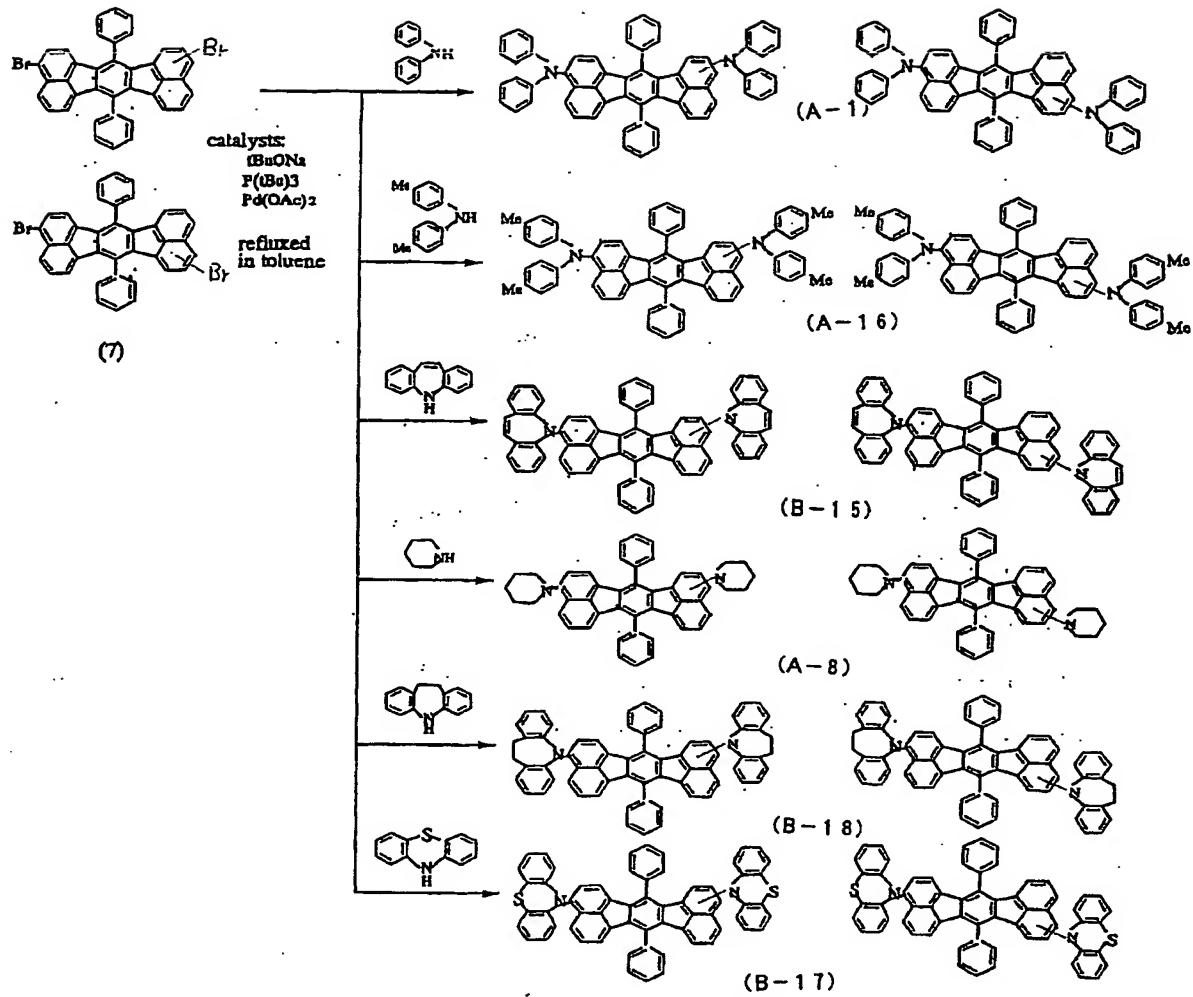
In accordance with the J. B. Allen's process, 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthenes (7) were synthesized using acenaphthenequinone (1) as the starting material via 7,14-diphenylacenaphtho[1,2-k]fluoranthene (6). The structures of 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthenes were identified from FD-MS (the field desorption mass spectra) and the <sup>1</sup>H-NMR spectra. The chemical shifts in <sup>1</sup>H-NMR agreed with the measured values reported by Allen (J. D. Debad, A. I. Bard, J. Chem. Soc., Vol. 120, 2476 (1998)).

**(B) Synthesis of 3,10- and 3,11-diphenylamino-7,14-diphenyl-acenaphthofluoranthenes (Compound A-1)**

Into 150 ml of toluene, 3.56 g (5.6 mmole) of 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthenes (7), 1.89 g (11.2

mmole) of diphenylamine, 0.06 g (0.3 mmole) of palladium acetate, 0.22 g (1.1 mmole) of tri-tert-butylphosphine and 1.51 g (14.0 mmole) of sodium tert-butoxide were dissolved at the room temperature and the reaction was allowed to proceed for 6 hours while the mixture was refluxed under heating. The resultant reaction mixture was filtered. The filtrate was concentrated and 4.8 g of a red orange powdery solid was obtained. After the solid was dissolved in toluene, the solution was fractionated in accordance with the column chromatography using a column packed with silica gel and 4.1 g of the main component was obtained. The main component was confirmed to be 3,10- and 3,11-diphenylamino-7,14-diphenylacenaphthofluoranthenes (Compound A-1) from FD-MS (812) and the structure of Compound (7). Precipitates in the reaction mixture separated by the filtration was washed with acetone and water and dried and 0.6 g of a powdery solid was obtained. The obtained solid was confirmed to have the same structure as that of the product obtained from the filtrate from FD-MS (812) and the <sup>1</sup>H-NMR spectrum.

Similarly, Compound A-16 (Synthesis Example 2), Compound B-15 (Synthesis Example 3), Compound A-8 (Synthesis Example 4), Compound B-18 (Synthesis Example 5) and Compound B-17 (Synthesis Example 6) which are compounds of 3,10- and 3,11-diamino-7,14-diphenylacenaphtho-[1,2-k]fluoranthenes were synthesized via the reaction routes shown in the following:



### Synthesis Example 2 (Compound A-16)

The reaction was conducted in accordance with the same procedures as those conducted in Synthesis Example 1 (B) except that 2.31 g (11.7 mmole) of p,p'-ditolylamine was used in place of diphenylamine. After the reaction was completed, the reaction mixture was filtered. The filtrate was washed with water and concentrated and a red powdery solid was obtained. The obtained solid was fractionated in accordance with the column chromatography using a column packed with silica gel and 2.9 g of the main component having a high purity was obtained. The main component was confirmed to be Compound A-16 from FD-MS (868).

### Synthesis Example 3 (Compound B-15)

The reaction was conducted in accordance with the same procedures as those conducted in Synthesis Example 1 (B) except that 2.27 g (11.7 mmole) of iminostilbene was used in place of diphenylamine. After the reaction was completed, the product precipitated in the reaction mixture was separated, repeatedly washed with acetone and water and dried and 3.4 g of a red orange powdery solid was obtained. The obtained solid was dissolved in tetrahydrofuran and fractionated in accordance with the thin layer chromatography using a thin layer of silica gel and 2.3 g of the main component having a high purity was obtained. The main component was confirmed to be Compound B-15 from FD-MS (862).

### Synthesis Example 4 (Compound A-8)

The reaction was conducted in accordance with the same procedures as those conducted in Synthesis Example 1 (B) except that 1.0 g (11.7

mmole) of piperidine was used in place of diphenylamine. After the reaction was completed, the reaction mixture was filtered. The filtrate was washed with water and concentrated and a red powdery solid was obtained. The obtained solid was dissolved in toluene and fractionated in accordance with the column chromatography using a column packed with silica gel and 2.1 g of the main component having a high purity was obtained. The main component was confirmed to be Compound A-8 from FD-MS (644).

#### Synthesis Example 5 (Compound B-18)

The reaction was conducted in accordance with the same procedures as those conducted in Synthesis Example 1 (B) except that 1.96 g (11.7 mmole) of carbazole was used in place of diphenylamine. After the reaction was completed, the product precipitated in the reaction mixture was separated, repeatedly washed with acetone and water and dried and 3.8 g of a red orange powdery solid was obtained. The obtained solid was dissolved in tetrahydrofuran and fractionated in accordance with the thin layer chromatography using a thin layer of silica gel and 2.0 g of the main component having a high purity was obtained. The main component was confirmed to be Compound B-18 from FD-MS (808).

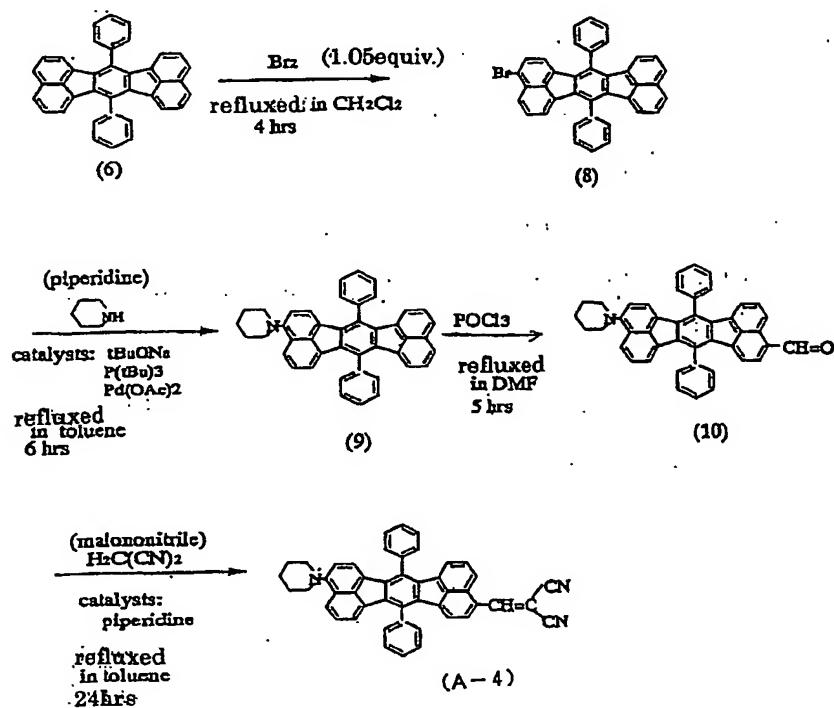
#### Synthesis Example 6 (Compound B-17)

The reaction was conducted in accordance with the same procedures as those conducted in Synthesis Example 1 (B) except that 2.33 g (11.7 mmole) of phenothiazine was used in place of diphenylamine. After the reaction was completed, the reaction mixture was filtered. The filtrate

was washed with water, concentrated and dried and 4.2 g of a orange powdery solid was obtained. The obtained solid was dissolved in toluene and fractionated in accordance with the thin layer chromatography using a layer of silica gel and 2.6 g of the main component having a high purity was obtained. The main component was confirmed to be Compound B-17 from FD-MS (872).

#### Synthesis Example 7 (Compound A-4)

Compound A-4 was synthesized via the reaction route shown in the following:



In the synthesis of Compound (8), the reaction mixture was examined in accordance with the thin layer chromatography and the reaction was allowed to continue until the spot of Compound (6) disappeared. After the reaction was completed, the reaction mixture was washed with a 0.1N aqueous solution of sodium hydroxide, concentrated and fractionated in accordance with the column chromatography using a column packed with silica gel and Compound (8) was obtained.

The reaction was conducted in accordance with the same procedures as those conducted in Synthesis Example 1 (B) except that 3.12 g (5.6 mmole) of Compound (8) was used in place of Compound (7) and 0.51 g (11.5 mmole) of piperidine was used in place of diphenylamine. The solid obtained by the reaction was dissolved in toluene and fractionated in accordance with the column chromatography using a column packed with silica gel and 2.2 g of Compound (9) having a high purity was obtained.

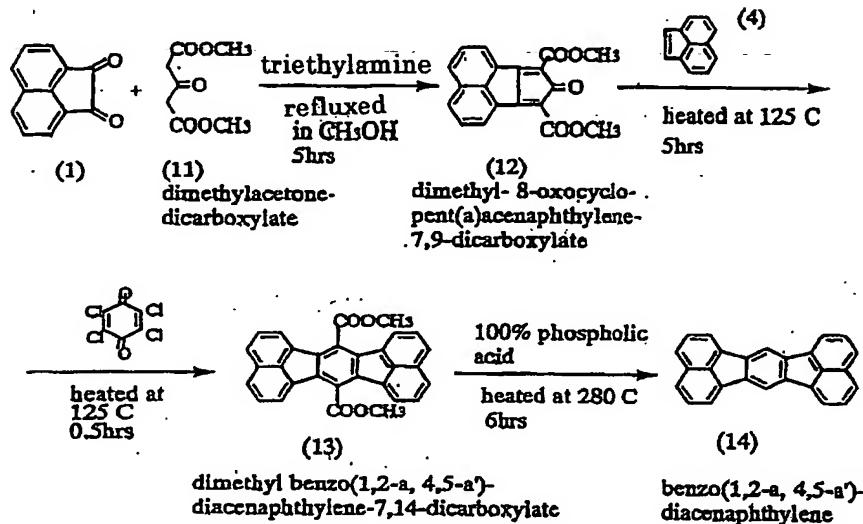
Compound (9) in an amount of 5.61 g (10.0 mmole) was dissolved into 30 ml of dimethylformamide. To the obtained solution, 1.68 g (11.0 mmole) of phosphorus oxychloride was added and the mixture was refluxed under heating. After the reaction was completed, the reaction mixture was filtered and the filtrate was fractionated in accordance with the column chromatography using a column packed with silica gel and 4.0 g of the main component having a high purity was obtained. The main component was confirmed to be Compound (10) from FD-MS (589).

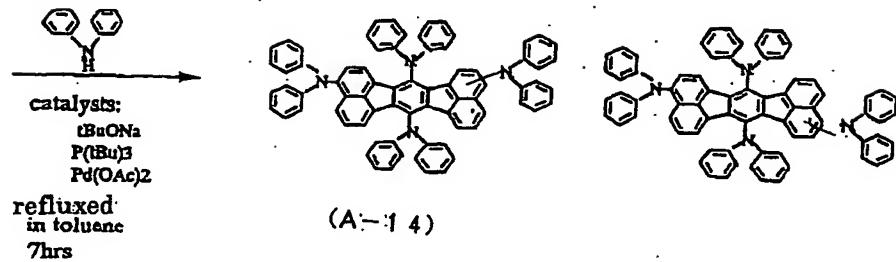
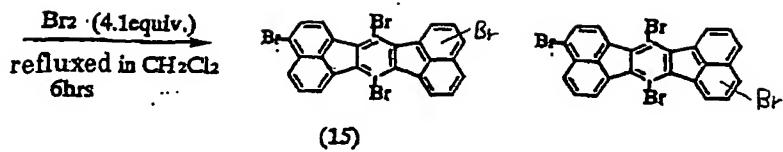
Compound (10) in an amount of 4.7 g (8.0 mmole) was reacted with 0.7 g (10.6 mmole) of malonitrile. The reaction product precipitated in the reaction mixture was separated and dissolved in tetrahydrofuran. The obtained solution was fractionated in accordance with the thin layer

chromatography using a thin layer of silica gel and 3.6 g of red orange crystals having a high purity were obtained. The crystals were confirmed to be Compound A-4 from FD-MS (637).

#### Synthesis Example 8 (Compound A-14)

Compound A-14 was synthesized via the reaction route shown in the following (S. H. Tucker, J. Chem. Soc., 1462 (1958)):

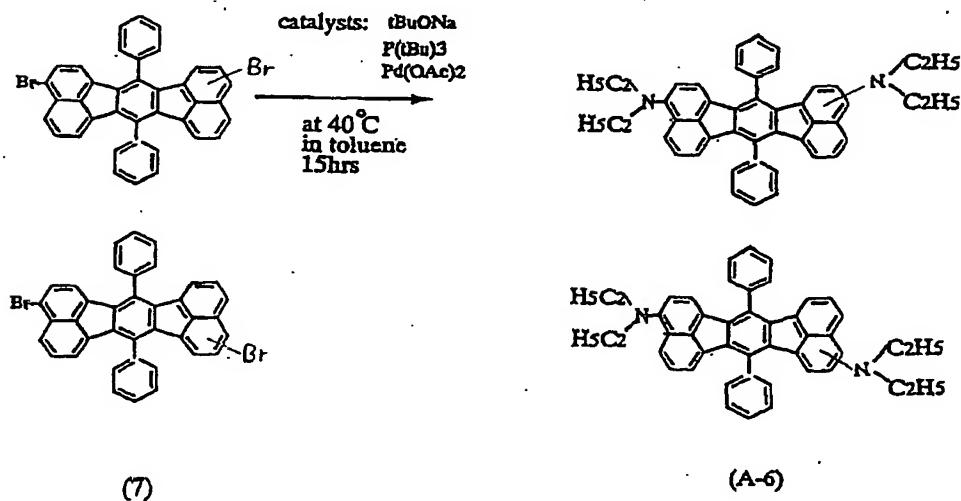




\* (1) → (14) cf. S. H. Tucker J. Chem. Soc. 1462 (1958)

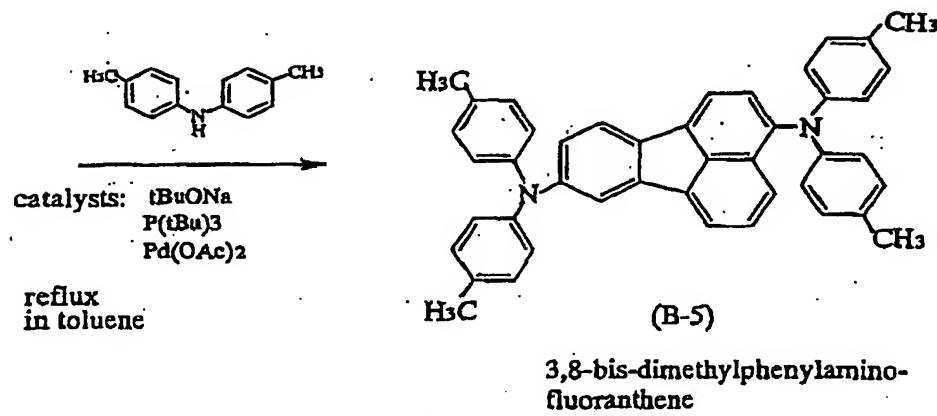
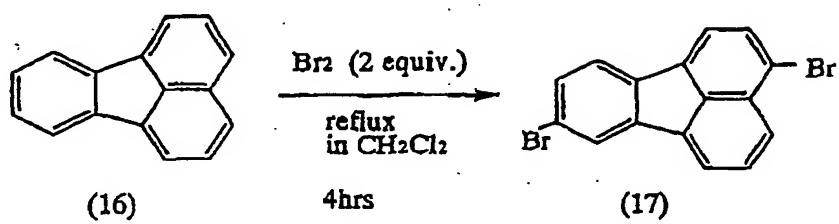
### Synthesis Example 9 (Compound A-6)

Compound A-6 was synthesized via the reaction route shown in the following:



Synthesis Example 10 (Compound B-5)

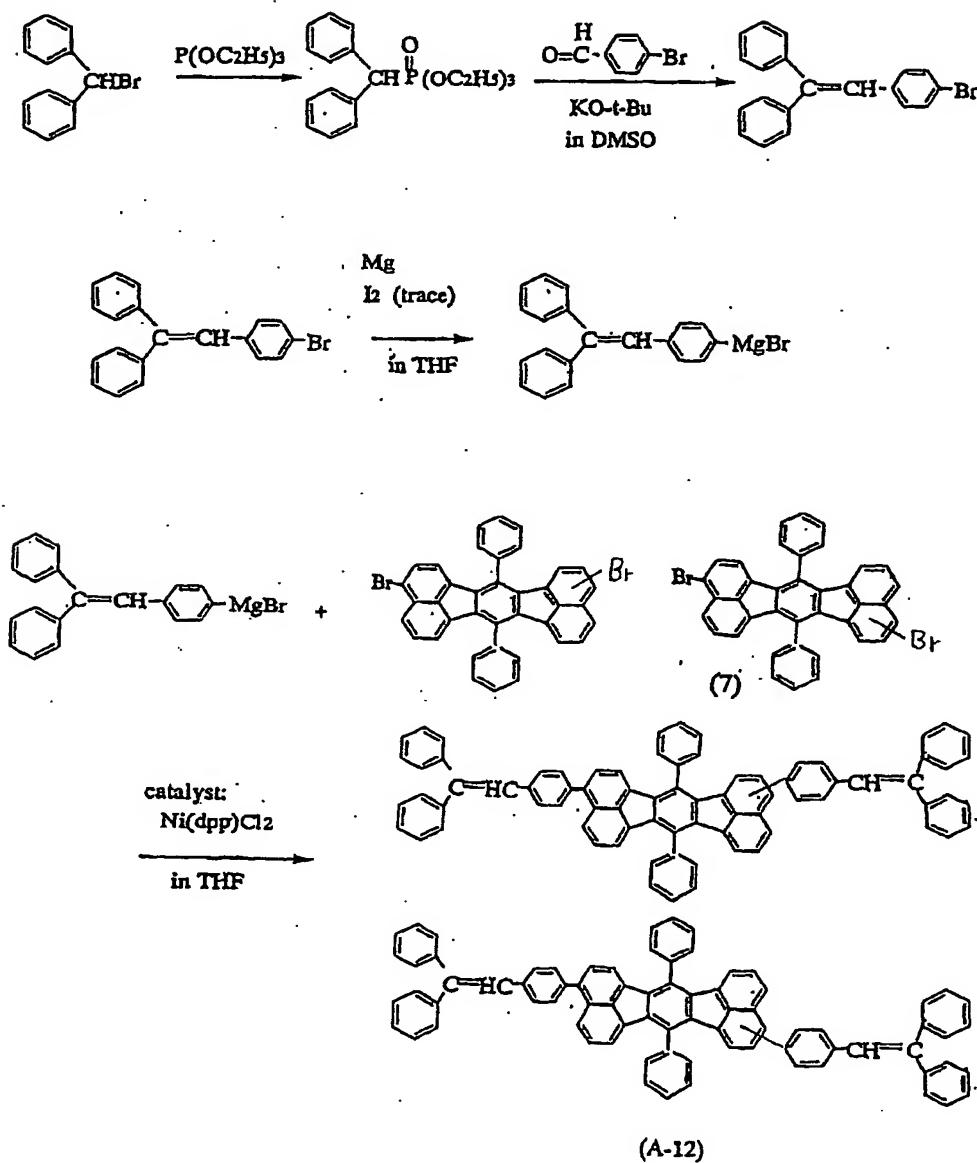
Compound B-5 was synthesized via the reaction route shown in the following (Beil. 5(3) 2278):



(16) : cf. Beil. 5(3) 2278

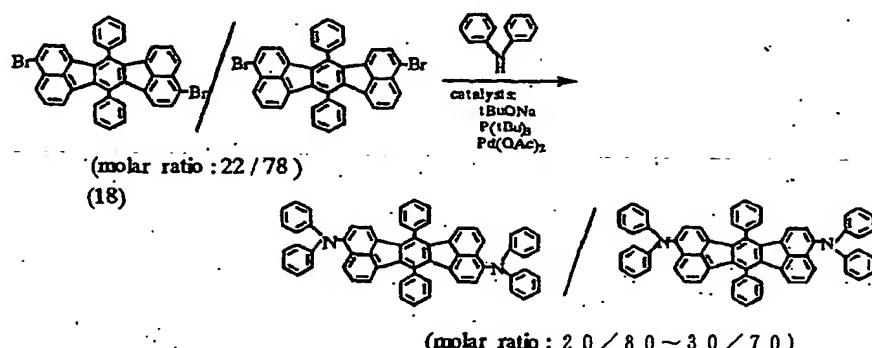
Synthesis Example 11 (Compound A-12)

Compound A-12 was synthesized via the reaction route shown in the following:



### Synthesis Example 12

A composition containing 3,10-bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthene and 3,11-bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthene in a ratio of the amounts by mole in the range of 20:80 to 30:70 was synthesized via the reaction route shown in the following:



(A) Synthesis of a composition (18) containing 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthenes in a ratio of the amounts by mole of 22:78

The solution portion of the reaction mixture obtained in Synthesis Example 1 (A) was concentrated, dissolved in tetrahydrofuran and recrystallized and the formed precipitates were removed. The solution portion was concentrated and a dibromo compound was obtained. This dibromo compound was confirmed to be a composition containing 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthenes in a ratio of the amounts by mole of 22:78 from the <sup>1</sup>H-NMR spectrum.

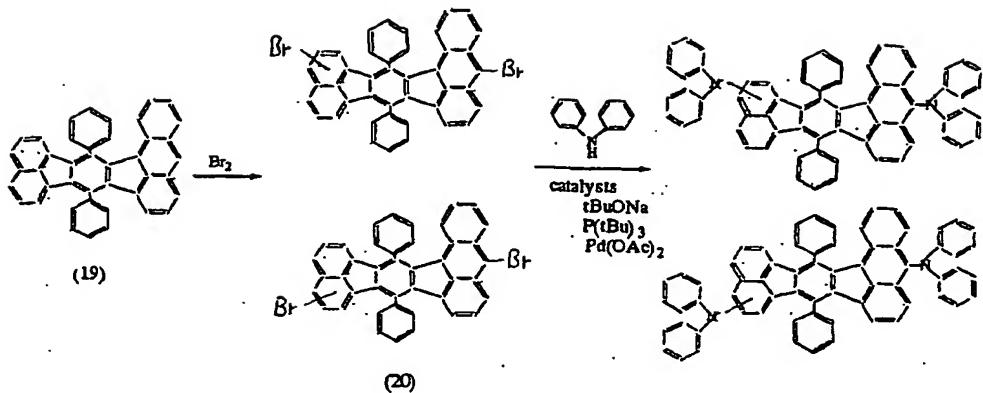
(B) Synthesis of a composition containing 3,10- and 3,11-bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthenes in a ratio

by the amounts by mole in the range of 20:80 to 30:70

Into 100 ml of toluene, 5.00 g (7.9 mmole) of the composition containing 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]-fluoranthenes in a ratio of the amounts by mole of 22:78 (18), 2.78 g (16.5 mmole) of diphenylamine, 0.09 g (0.09 mmole) of palladium acetate, 0.44 g (2.2 mmole) of tri-tert-butylphosphine and 2.12 g (19.6 mmole) of sodium tert-butoxide were dissolved and the reaction was allowed to proceed for 6 hours while the mixture was refluxed under heating. After the reaction was completed, the reaction mixture was filtered. The filtrate was concentrated and fractionated in accordance with the column chromatography using a column packed with silica gel and 6.20 g of a red orange powdery solid was obtained. This solid was confirmed to be a composition containing 3,10-bisdiphenylamino-7,14-diphenylacenaphtho-[1,2-k]fluoranthene and 3,11-bisdiphenylamino-7,14-diphenylacenaphtho-[1,2-k]fluoranthene in a ratio of the amounts by mole in the range of 20:80 to 30:70 from FD-MS (812) and the <sup>1</sup>H-NMR spectrum (H: 400 MHz; the solvent of the measurement: DMSO (120°C); shown in Figure 1).

#### Synthesis Example 13

5,12- and/or 5,13-Bisdiphenylamino-9,16-diphenylfluorantheno[8,9-a]aceanthrylenes were synthesized via the reaction route shown in the following:



(A) Synthesis of 9,16-diphenylfluorantheno[8,9-a]aceanthrylene (19)

With reference to the Bandyopadhyai's process, 9,16-diphenylfluorantheno[8,9-a]aceanthrylene was synthesized by the reaction of 1,3-diphenylcyclopenta[a]aceanthrylen-2-one and acenaphthylene using aceanthrylenequinone as the starting material [Indian J. Chem., Vol. 21B, 91 (1982)].

(B) Synthesis of 5,12- and/or 5,13-dibromo-9,16-diphenyl-fluorantheno[8,9-a]aceanthrylene (20)

Into 240 ml of methylene chloride, 4.00 g (7.6 mmole) of 9,16-diphenylfluorantheno[8,9-a]aceanthrylene (19) was dissolved. While the obtained mixture was refluxed under heating, 18.0 ml of a 1M methylene chloride solution of bromine was added dropwise and the reaction was allowed to proceed for 2 hours. The resultant reaction mixture was washed with an aqueous solution of sodium hydroxide and pure water and concentrated and 5.06 g of a yellow brown powdery solid was obtained. The solid was confirmed to be 5,12-dibromo-9,16-diphenyl-fluorantheno[8,9-a]aceanthrylene and/or 5,13-dibromo-9,16-diphenyl-fluorantheno[8,9-a]aceanthrylene from FD-MS (686) and the <sup>1</sup>H-NMR

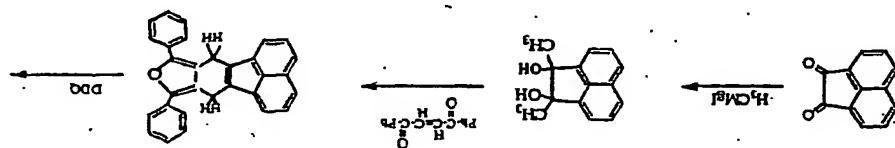
spectrum.

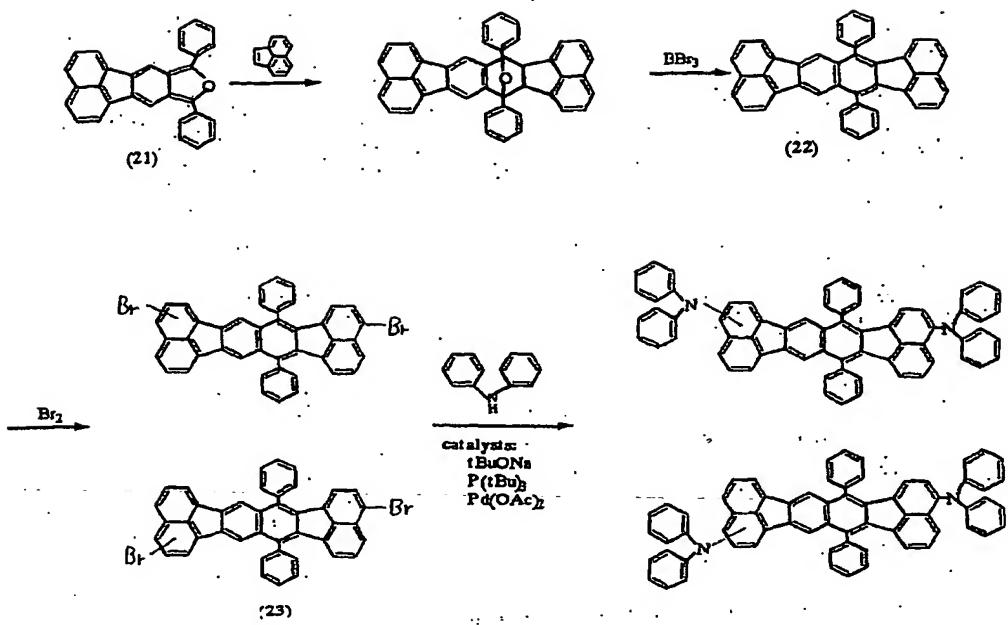
(C) Synthesis of 5,12- and/or 5,13-bisdiphenylamino-9,16-diphenylfluorantheno[8,9-a]aceanthrylene

Into 200 ml of toluene, 5.00 g (7.4 mmole) of 5,12- and/or 5,13-dibromo-9,16-diphenylfluorantheno[8,9-a]aceanthrylene (20), 2.75 g (16.2 mmole) of diphenylamine, 0.09 g (0.4 mmole) of palladium acetate, 0.43 g (2.2 mmole) of tri-tert-butylphosphine and 2.05 g (20.6 mmole) of sodium tert-butoxide were dissolved and the reaction was allowed to proceed for 5 hours while the mixture was refluxed under heating. After the reaction was completed, the reaction mixture was filtered. The filtrate was concentrated and fractionated in accordance with the column chromatography using a column packed with silica gel and 4.27 g of a black purple powdery solid of the main component was obtained. The main component was confirmed to be 5,12- and/or 5,13-bisdiphenylamino-9,16-diphenylfluorantheno[8,9-a]aceanthrylene from FD-MS (862) and the <sup>1</sup>H-NMR spectrum (H: 400 MHz; the solvent of the measurement: DMSO (120°C); shown in Figure 2).

Synthesis Example 14

3,11- and/or 3,12-Bisdiphenylamino-7,16-diphenylfluorantheno[8,9-k]fluoranthene was synthesized via the reaction route shown in the following:





(A) Synthesis of 2,5-diphenylfluorantheno[11',12':3,4]furan (21)

In accordance with the N. Campbell's process [J. Chem. Soc., 1555 (1949)], 2,5-diphenylfluorantheno[11',12':3,4]furan (21) was synthesized by the reaction of 7,8-dimethylacenaphthene-7,8-diol which was synthesized in accordance with the S. H. Tucker's process [J. Chem. Soc., 1462 (1958)] and trans-1,2-dibenzoylethylene.

(B) Synthesis of 7,16-diphenylfluorantheno[8,9-k]fluoranthenene (22)

Into a mixed solvent containing 500 ml of xylene and 660 ml of methylene chloride, 5.00 g (12.7 mmole) of 2,5-diphenylfluorantheno[11',12':3,4]furan (21) and 3.86 g (19.0 mmole) of acenaphthylene were added and the mixture was refluxed under heating for 3 hours. The solution was cooled and 16.0 ml of a 1M methylene chloride solution of  $BBr_3$  was added dropwise to the cooled solution. The obtained solution

was heated at 60°C for 4 hours. The resultant reaction mixture was washed with an aqueous solution of sodium hydrogencarbonate and pure water, concentrated and purified in accordance with the column chromatography using a column packed with silica gel and 3.20 g of yellow crystals were obtained. The crystals were confirmed to be 7,16-diphenylfluorantheno[8,9-k]fluoranthene (22) from FD-MS (528) and the <sup>1</sup>H-NMR spectrum.

(C) Synthesis of 3,11- and/or 3,12-dibromo-7,16-diphenylfluorantheno[8,9-k]fluoranthene (23)

Into 230 ml of methylene chloride, 2.30 g (4.3 mmole) of 7,16-diphenylfluorantheno[8,9-k]fluoranthene (22) was dissolved. While the obtained solution was refluxed under heating, 9.0 ml of a 1M methylene chloride solution of bromine was added dropwise to the solution and then the reaction was allowed to proceed for 2 hours. The resultant reaction mixture was washed with an aqueous solution of sodium hydroxide and pure water and concentrated and 3.06 g of a light yellow brown crystals were obtained. The crystals were confirmed to be 3,11- and/or 3,12-dibromo-7,16-diphenylfluorantheno[8,9-k]fluoranthene (23) from FD-MS (686) and the <sup>1</sup>H-NMR spectrum.

(D) Synthesis of 3,11- and/or 3,12-bis(diphenylamino)-7,16-diphenylfluorantheno[8,9-k]fluoranthene

Into 120 ml of toluene, 3.92 g (5.7 mmole) of 3,11- and/or 3,12-dibromo-7,16-diphenylfluorantheno[8,9-k]fluoranthene (23), 2.03 g (12.0 mmole) of diphenylamine, 0.07 g (0.07 mmole) of palladium acetate, 0.33 g (1.7 mmole) of tri-tert-butylphosphine and 1.56 g (14.4 mmole) of sodium tert-butoxide were dissolved and the reaction was allowed to

proceed for 6 hours while the mixture was refluxed under heating. After the reaction was completed, the reaction mixture was filtered. The filtrate was purified in accordance with the column chromatography using a column packed with silica gel and 4.27 g of orange powdery crystals were obtained. The crystals were confirmed to be 3,11- and/or 3,12-bis diphenylamino-7,16-diphenylfluorantheno[8,9-k]fluoranthene from FD-MS (862) and the <sup>1</sup>H-NMR spectrum (H: 400 MHz; the solvent of the measurement: DMSO (120°C); shown in Figure 3).

#### Synthesis Example 15

A composition containing 3,10-bisditolylamino-7,14-diphenyl-acenaphtho[1,2-k]fluoranthene and 3,11-bisditolylamino-7,14-diphenyl-acenaphtho[1,2-k]fluoranthene in a ratio of the amounts by mole in the range of 80:20 to 90:10 was synthesized.

(A) Synthesis of a composition (18) containing 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthenes

The solution portion of the reaction mixture obtained in Synthesis Example 1 (A) was concentrated, dissolved entirely in tetrahydrofuran and recrystallized and the formed precipitates were removed. The solution portion was concentrated and a dibromo compound was obtained. This dibromo compound was confirmed to be a composition containing 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthenes containing in a ratio of the amounts by mole in the range of 80:20 to 90:10 from the <sup>1</sup>H-NMR spectrum.

(B) Synthesis of a composition containing 3,10- and 3,11-bisditolylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthenes in a ratio of

the amounts by mole in the range of 80:20 to 90:10

In accordance with the same procedures as those conducted in Synthesis Example 12 (B) except that di-p,p-tolylamine was used in place of diphenylamine, a composition (A-16) containing 3,10- and 3,11-bisditolylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthenes in a ratio of the amounts by mole in the range of 80:20 to 90:10 was synthesized.

#### Synthesis Example 16

A composition containing 3,10-bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthene and 3,11-bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthene in a ratio of the amounts by mole in the range of 80:20 to 90:10 was synthesized.

(A) Synthesis of a composition (18) containing 3,10- and 3,11-dibromo-7,14-diphenylacenaphtho[1,2-k]fluoranthenes

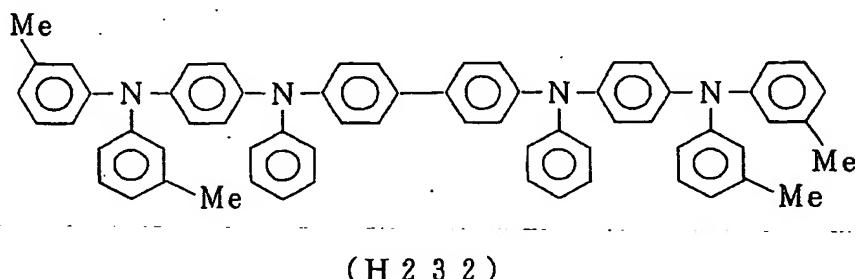
The composition containing the dibromo compounds was obtained in accordance with the same procedures as those conducted in Synthesis Example 15 (A).

(B) Synthesis of a composition (A-1) containing 3,10- and 3,11-bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthenes in a ratio of the amounts by mole in the range of 80:20 to 90:10

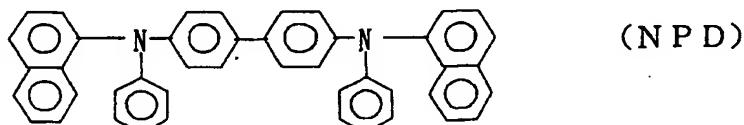
In accordance with the same procedures as those conducted in Synthesis Example 12 (B) using the composition obtained above in (A), a composition containing 3,10-bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthene and 3,11-bisdiphenylamino-7,14-diphenylacenaphtho[1,2-k]fluoranthene in a ratio of the amounts in mole in the range of 80:20 to 90:10 was synthesized.

**Example 1**

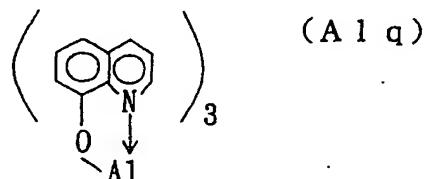
On a cleaned glass plate having an ITO electrode, the following compound (H232) as the hole injecting material was vapor deposited so that a film having a thickness of 60 nm was formed.



Then, the following compound (NPD) as the hole transporting material was vapor deposited so that a film having a thickness of 20 nm was formed.



Subsequently, an aluminum complex of 8-hydroxyquinoline (Alq) and 3,10- and 3,11-diphenylamino-7,14-diphenylacenaphthofluoranthenes (Compound A-1) as the materials for the light emitting layer were vapor deposited so that a film containing 2.1% by mole of Compound A-1 and having a thickness of 50 nm was formed. The structure of Alq is shown in the following:



An electron injecting layer was formed by vapor deposition of Alq alone so that the formed film had a thickness of 10 nm. A layer of an inorganic compound was formed on the electron injecting layer by vapor deposition of LiF so that the formed film had a thickness of 0.2 nm. On the thus formed layer, aluminum was vapor deposited so that an electrode having a thickness of 170 nm was formed and an organic EL device was obtained. The vapor depositions for forming the above layers were conducted under  $10^{-6}$  Torr while the substrate was kept at the room temperature.

The light emitting property of this device was as follows: the luminance under application of a direct current of 5.5 V: 103 cd/m<sup>2</sup>; the efficiency of light emission: as high as 6.2 cd/A. The emitted light was orange light having chromaticity coordinates of (0.56, 0.44). When the device was driven under a constant current at an initial luminance of 500 cd/m<sup>2</sup>, the half-life was as long as 2600 hours.

This example shows that an organic EL device exhibiting a high performance can be obtained by using Compound A-1 as the doping material. The spectrum of the light emitted by the device was obtained and found to be the same as the fluorescence spectrum of the doping material. Thus, it is shown that the doping material worked as the center of light emission.

#### Comparative Example 1

An organic EL device was obtained in accordance with the same procedures as those conducted in Example 1 except that rubrene was vapor deposited in place of Compound A-1 so that a film containing 4.0% by mole of rubrene was formed.

The light emitting property of this device was as follows: the luminance under application of a direct current of 5.5 V: 105 cd/m<sup>2</sup>; the efficiency of light emission: 7.6 cd/A. However, the emitted light was yellow light having chromaticity coordinates of (0.50, 0.50). The half-life was 1000 hours when the device was driven under a constant current at an initial luminance of 500 cd/m<sup>2</sup> and shorter than that of the device of Example 1.

#### Comparative Example 2

An organic EL device was obtained in accordance with the same procedures as those conducted in Example 1 except that fluorantheno[8,9-k]fluoranthene described in Japanese Patent Application Laid-Open No. Heisei 11(1999)-40360 was vapor deposited in place of Compound A-1 so that a film containing 2% by mole of this fluoranthene was formed.

The light emitting property of this device was as follows: the luminance under application of a direct current of 5.5 V: 35 cd/m<sup>2</sup>; the efficiency of light emission: 3.0 cd/A. The emitted light was yellow green light. The half-life was as short as 300 hours when the device was driven under a constant current at an initial luminance of 500 cd/m<sup>2</sup>.

#### Comparative Example 3

An organic EL device was obtained in accordance with the same procedures as those conducted in Example 1 except that 7,14-diphenylacenaphtho[1,2-k]fluoranthene described in Japanese Patent Application Laid-Open No. Heisei 11(1999)-168445 was vapor deposited in place of Compound A-1 so that a film containing 2% by mole of this

fluoranthene was formed.

The light emitting property of this device was as follows: the luminance under application of a direct current of 6 V: 69 cd/m<sup>2</sup>; the efficiency of light emission: 1.3 cd/A. The emitted light was yellow green light. The efficiency was smaller than that of a device in which Alq alone was used as the light emitting material. The half-life was as short as 400 hours when the device was driven under a constant current at an initial luminance of 500 cd/m<sup>2</sup>. When the spectrum of the light emitted by the device was obtained, the spectrum did not agree with the fluorescence spectrum of the doping material. Thus, it was found that the above compound did not emit light and the yellow green light was emitted from Alq. The doping material did not work as the light emitting material.

#### Examples 2 to 11

Organic EL devices were obtained in accordance with the same procedures as those conducted in Example 1 except that compounds shown in Table 1 were vapor deposited in place of Compound A-1.

The light emitting properties of these devices were obtained in accordance with the same methods as those used in Example 1. The voltage applied in the measurements, the luminance, the efficiency of light emission, the color of the emitted light and the half-life when the device was driven under a constant current at an initial luminance of 500 cd/m<sup>2</sup> are shown in Table 1.

#### Example 12

An organic EL device was obtained in accordance with the same

procedures as those conducted in Example 1 except that the composition containing the prescribed relative amounts of the isomers which was obtained in Synthesis Example 12 (Compound A-1) was used for the light emitting layer in a concentration of 100% and Alq was not used.

The light emitting property of this device was as follows: the luminance under application of a direct current of 4.5 V: 80 cd/m<sup>2</sup>; the efficiency of light emission: 3.5 cd/A. The half-life was as long as 2100 hours when the device was driven under a constant current at an initial luminance of 500 cd/m<sup>2</sup>. The device had a longer life than that of the device of Example 1 and can be used also as the main light emitting material.

#### Example 13

An organic EL device was obtained in accordance with the same procedures as those conducted in Example 1 except that the composition containing the prescribed relative amounts of the isomers which was obtained in Synthesis Example 15 (Compound A-16) was used for the light emitting layer in place of Compound A-1.

The light emitting property of this device was as follows: the luminance under application of a direct current of 5.5 V: 94 cd/m<sup>2</sup>; the efficiency of light emission: 5.94 cd/A. The emitted light was reddish orange light having chromaticity coordinates of (0.60, 0.39). The half-life was as long as 3200 hours when the device was driven under a constant current at an initial luminance of 500 cd/m<sup>2</sup>.

#### Example 14

An organic EL device was obtained in accordance with the same procedures as those conducted in Example 1 except that the composition containing the prescribed relative amounts of the isomers which was obtained in Synthesis Example 16 (Compound A-1) was used for the light emitting layer in place of Compound A-1.

The light emitting property of this device was as follows: the luminance under application of a direct current of 6 V: 100 cd/m<sup>2</sup>; the efficiency of light emission: 4.75 cd/A. The emitted light had chromaticity coordinates of (0.58, 0.42). The half-life was as long as 1800 hours when the device was driven under a constant current at an initial luminance of 500 cd/m<sup>2</sup>. The light having more reddish color than that of the light emitted in Example 1 could be emitted by using the above compound. This result was obtained because the composition contained a greater amount of the isomer 3,11-bisdiphenylamino-7,14-diphenylacenaphtho[12-k]fluoranthene which could emit light having a longer wavelength.

Table 1

	Compound	Voltage (V)	Luminance (cd/m <sup>2</sup> )	Efficiency of light emission (cd/A)	Color of emitted light	Half-life (hour)
Example 2	A-2	5.5	140	5.7	reddish orange	2800
Example 3	A-8	5.8	120	3.6	orange	2100
Example 4	A-14	5.2	120	6.1	red	2700
Example 5	A-16	6.0	170	4.7	reddish orange	3100
Example 6	B-3	6.0	160	3.2	reddish orange	1900
Example 7	B-15	5.5	130	2.8	orange	1800
Example 8	B-17	5.8	110	2.0	reddish orange	1700
Example 9	B-18	6.1	120	2.8	reddish orange	2000
Example 10	A-4	7.2	110	3.7	red	1000
Example 11	B-5	6.0	120	6.7	yellowish green	1800

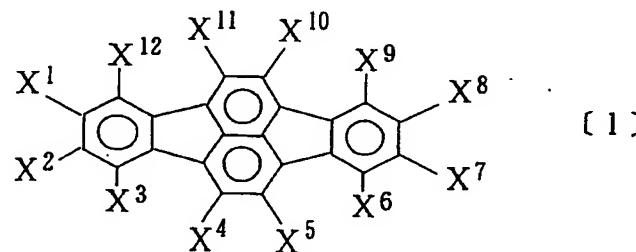
INDUSTRIAL APPLICABILITY

As described above in detail, the organic electroluminescence device of the present invention which utilizes the compound selected from the compounds represented by general formulae [1] to [18] emits yellowish to reddish light, exhibits an excellent purity of color and a high efficiency of light emission and has a long life.

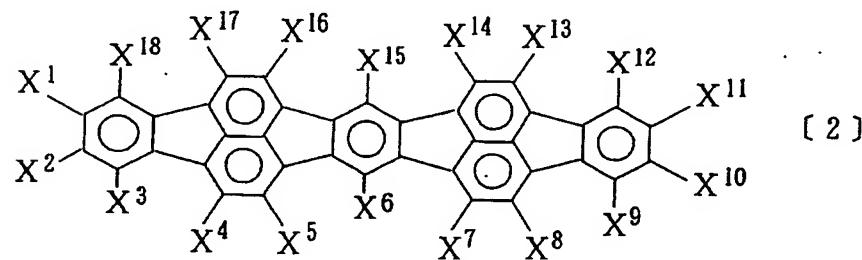
Therefore, the organic electroluminescence device of the present invention is advantageously used as a light source such as a planar light emitting member of televisions and a back light of displays.

## CLAIMS

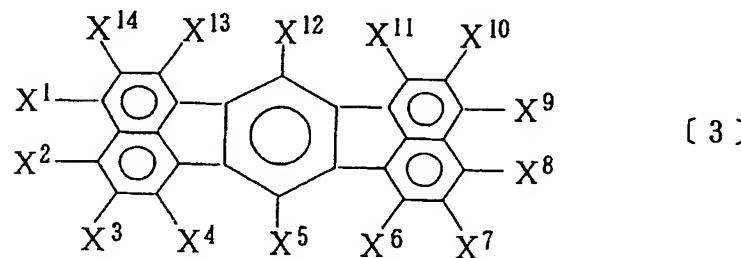
1. An organic electroluminescence device which comprises an organic layer disposed between at least one pair of electrodes, wherein the organic layer comprises a compound having a fluoranthene skeleton structure substituted at least with an amine group or an alkenyl group.
2. An organic electroluminescence device according to Claim 1, wherein said compound is a compound selected from compounds represented by the following general formulae [1] to [18]:



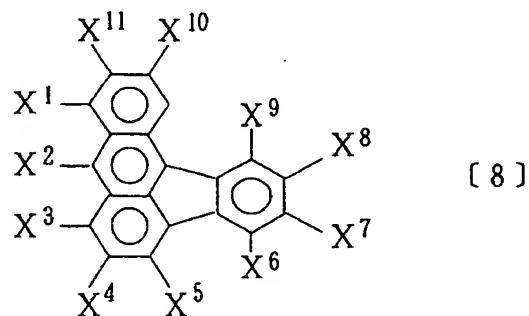
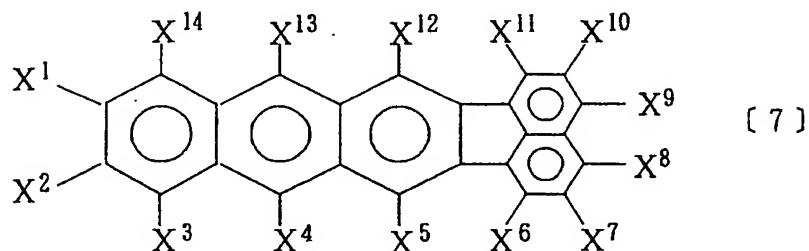
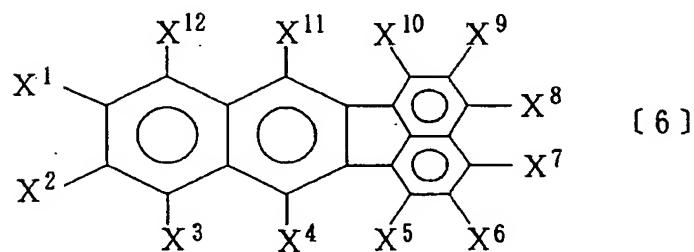
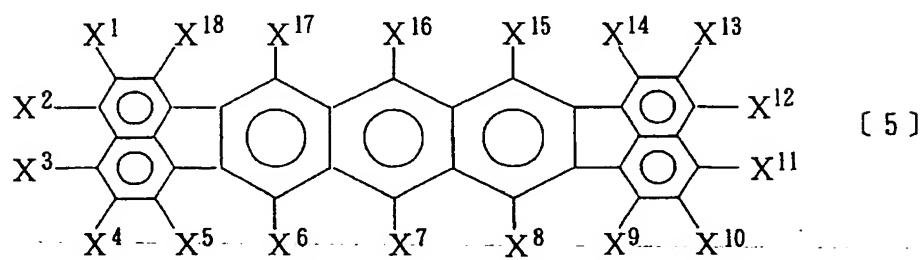
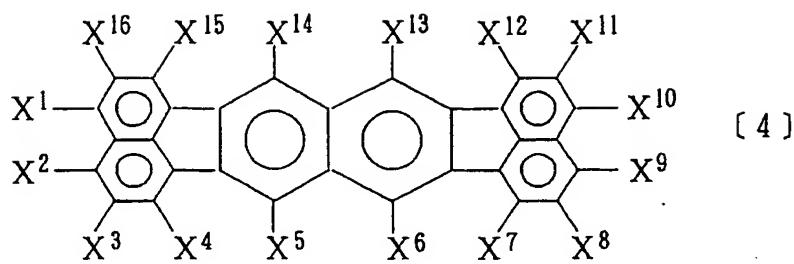
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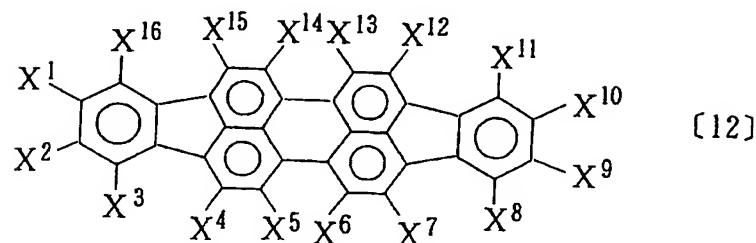
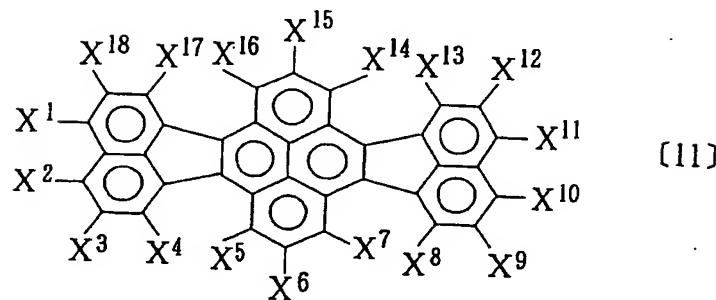
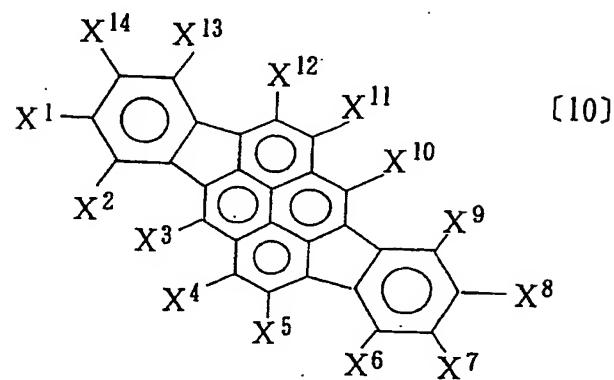
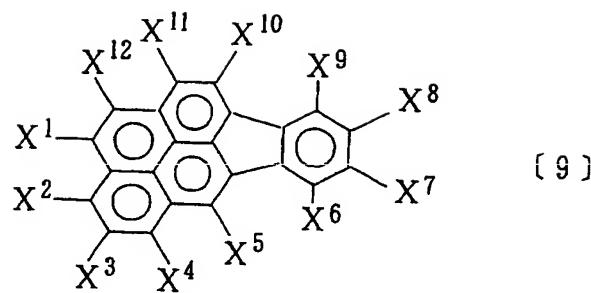


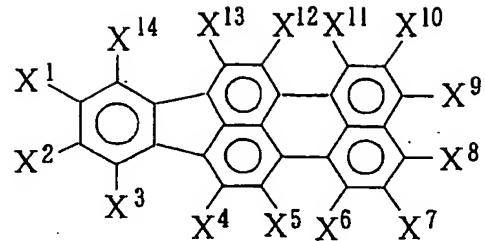
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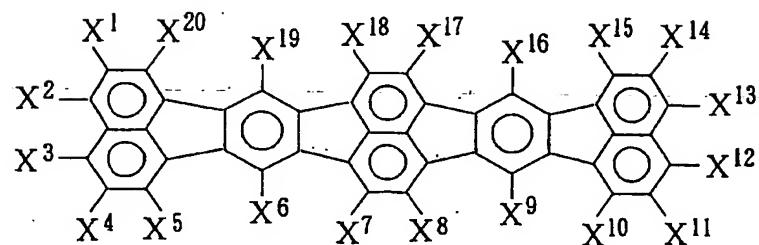
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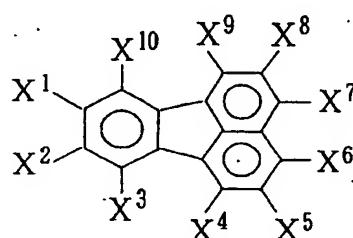




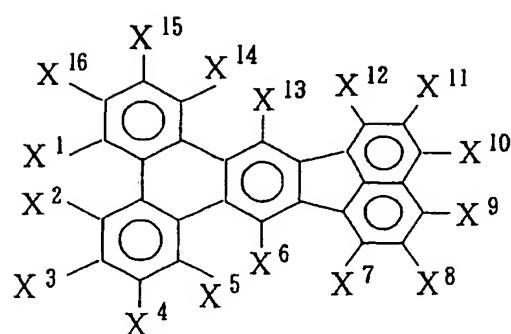
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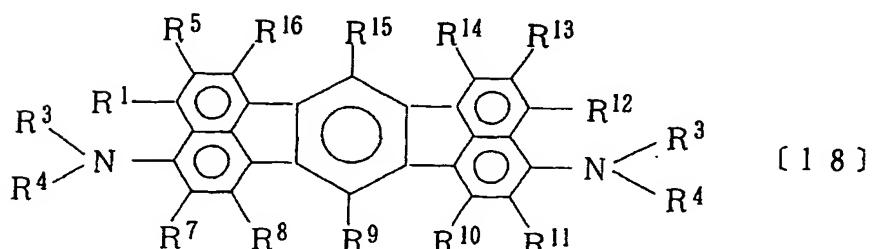
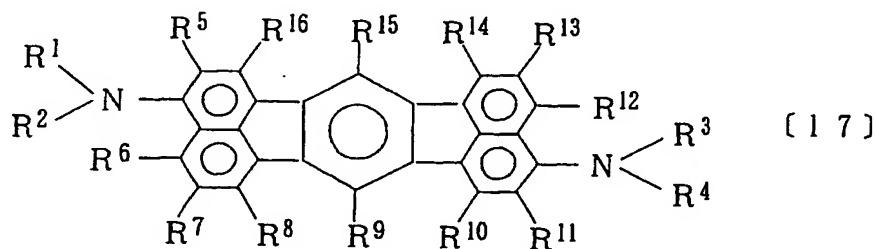


[15]



[16]

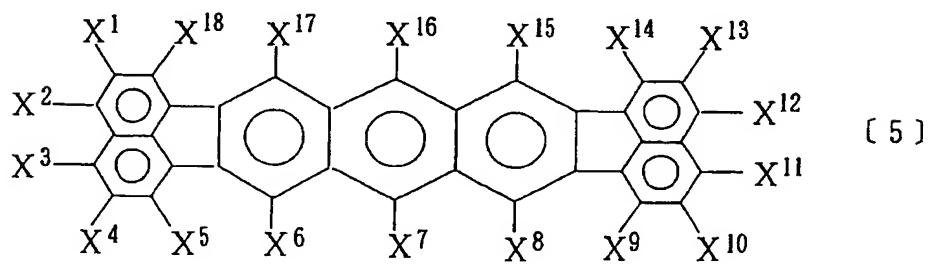
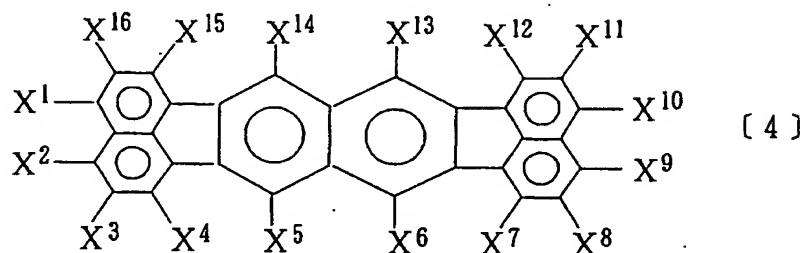
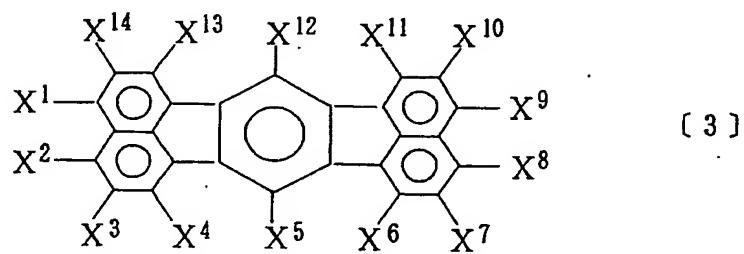
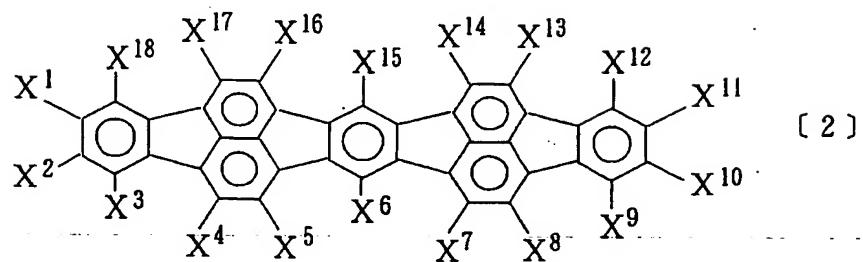
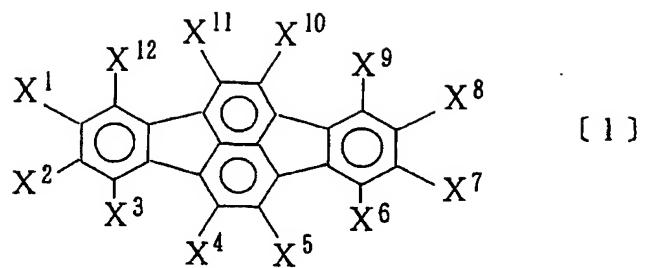
wherein X<sup>1</sup> to X<sup>20</sup> each independently represents hydrogen atom, a linear, branched or cyclic alkyl group having 1 to 20 carbon atoms, a linear, branched or cyclic alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon groups, a substituted or unsubstituted arylamino group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 30 carbon atoms, a substituted or unsubstituted arylalkylamino group having 7 to 30 carbon atoms or a substituted or unsubstituted alkenyl groups having 8 to 30 carbon atoms; a pair of adjacent groups represented by X<sup>1</sup> to X<sup>20</sup> and a pair of adjacent substituents to groups represented by X<sup>1</sup> to X<sup>20</sup> may form a cyclic structure in combination; when a pair of adjacent substituents are aryl groups, the pair of substituents may be a single group; and at least one of substituents represented by X<sup>1</sup> to X<sup>i</sup>, i representing a number of 12 to 20, comprises an amine group or an alkenyl group;

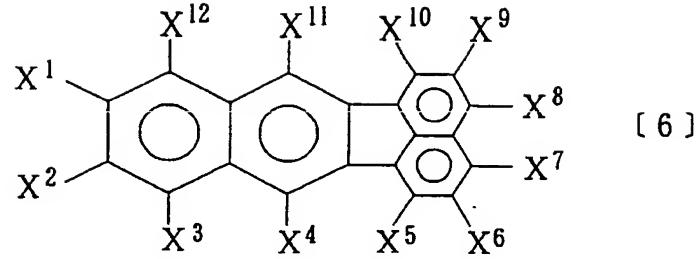


wherein R<sup>1</sup> to R<sup>4</sup> each independently represent an alkyl group having 1 to 20 carbon atoms or a substituted or unsubstituted aryl group having 6 to 30 carbon atoms; in one or both of a pair of groups represented by R<sup>1</sup> and R<sup>2</sup> and a pair of groups represented by R<sup>3</sup> and R<sup>4</sup>, the groups forming the pair may be bonded through -O- or -S-; R<sup>5</sup> to R<sup>16</sup> represents hydrogen atom, a linear, branched or cyclic alkyl group having 1 to 20 carbon atoms, a linear, branched or cyclic alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon groups, a substituted or unsubstituted arylamino group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 30 carbon atoms, a substituted or unsubstituted arylalkylamino group having 7 to 30 carbon atoms or a substituted or unsubstituted alkenyl groups having 8 to 30 carbon atoms; a pair of adjacent groups represented by R<sup>5</sup> to R<sup>16</sup> and a pair of adjacent substituents to groups represented by R<sup>5</sup> to R<sup>16</sup> may form a cyclic structure in combination; and at least one of substituents represented by R<sup>5</sup> to R<sup>16</sup> comprises an amine group or an alkenyl group.

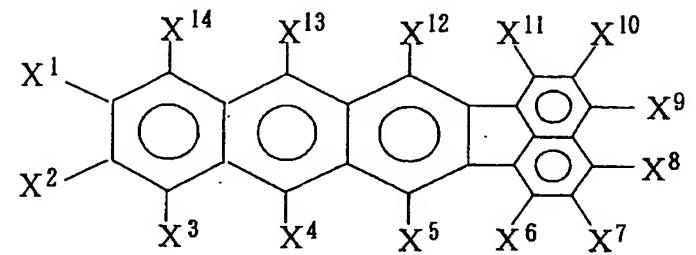
- ( ) 3. An organic electroluminescence device according to any of Claims 1 and 2, wherein the organic layer is at least one of a hole transporting layer and a light emitting layer.
4. An organic electroluminescence device according to Claim 1, wherein the organic layer comprises 1 to 70% by weight of said compound which is selected from compounds represented by general formulae [1] to [18].

5. An organic electroluminescence device according to any of Claims 1 to 4, wherein a layer of an inorganic compound is disposed between the organic layer and the electrode.
6. An organic electroluminescence device according to any of Claims 1 to 5, which emits reddish light.
7. An organic electroluminescence device according to Claim 1, wherein the organic layer comprises said compound and isomers thereof.
8. An organic electroluminescence device according to Claim 7, wherein, among said compound and the isomers thereof, a ratio of an amount by mole of an isomer which can emit light having a longer wavelength to an amount by mole of an isomer which can emit light having a shorter wave is in a range of 90:10 to 60:40.
9. An organic electroluminescence device according to Claim 7, wherein, among said compound and the isomers thereof, a ratio of an amount by mole of an isomer represented by general formula [17] to an amount by mole of an isomer represented by general formula [18] is in a range of 90:10 to 60:40.
10. A novel compound represented by any of the following general formulae [1] to [18]:

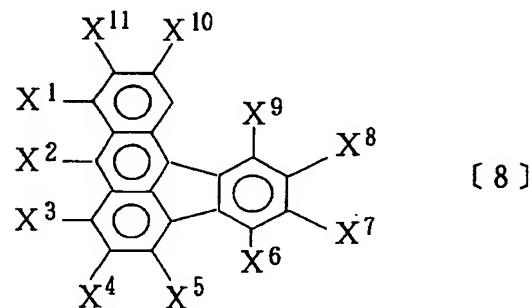




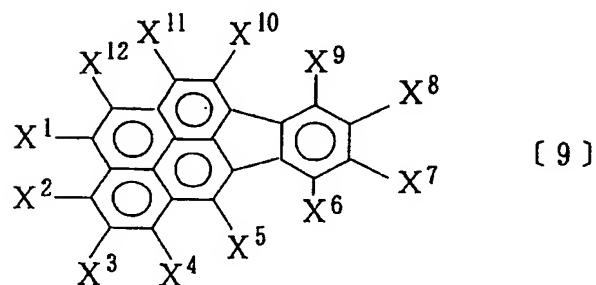
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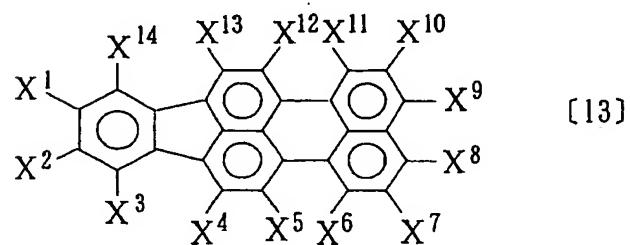
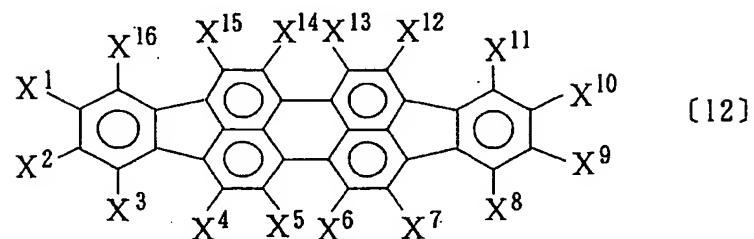
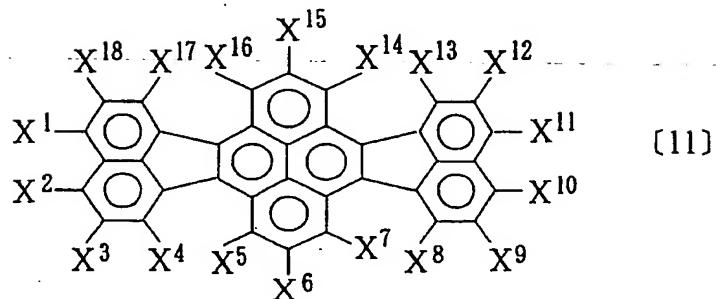
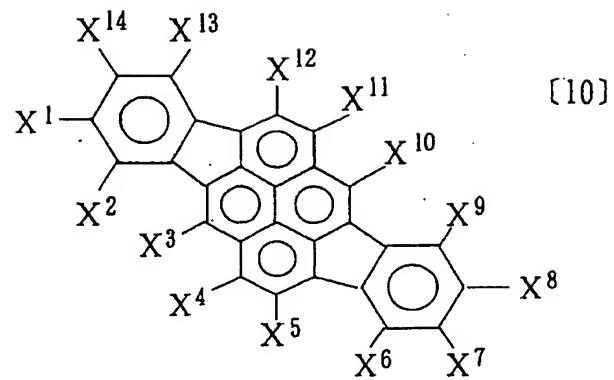
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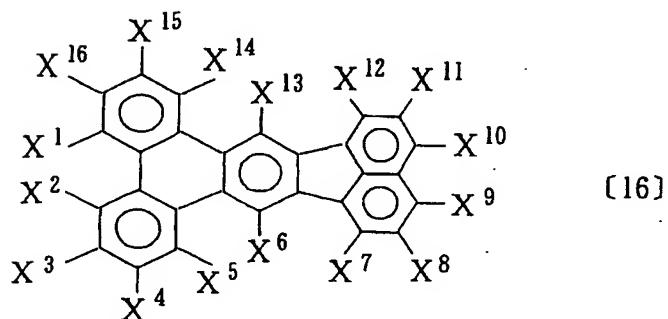
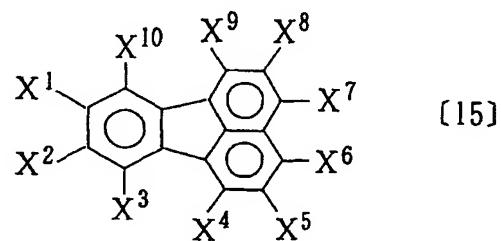
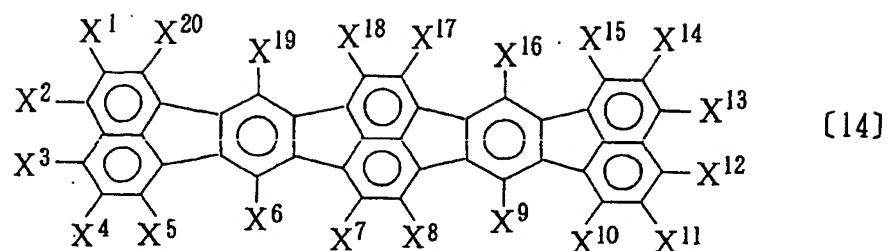


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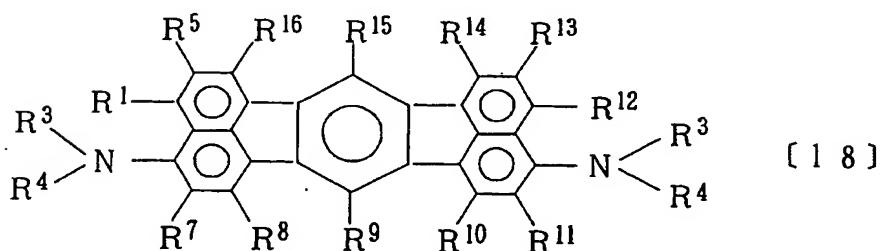
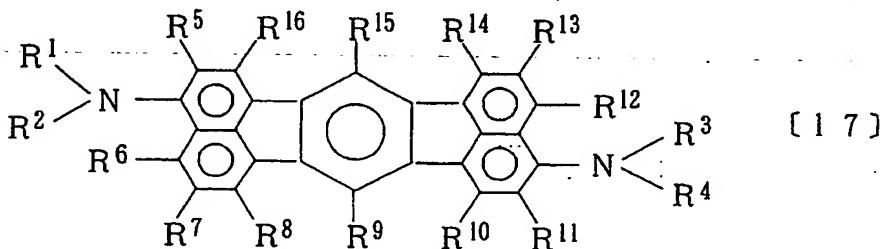
[ 9 ]





wherein X<sup>1</sup> to X<sup>20</sup> each independently represents hydrogen atom, a linear, branched or cyclic alkyl group having 1 to 20 carbon atoms, a linear, branched or cyclic alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon groups, a substituted or unsubstituted arylamino group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 30 carbon atoms, a

substituted or unsubstituted arylalkylamino group having 7 to 30 carbon atoms or a substituted or unsubstituted alkenyl groups having 8 to 30 carbon atoms; a pair of adjacent groups represented by X<sup>1</sup> to X<sup>20</sup> and a pair of adjacent substituents to groups represented by X<sup>1</sup> to X<sup>20</sup> may form a cyclic structure in combination; when a pair of adjacent substituents are aryl groups, the pair of substituents may be a single group; and at least one of substituents represented by X<sup>1</sup> to X<sup>i</sup>, i representing a number of 12 to 20, comprises an amine group or an alkenyl group;



wherein R<sup>1</sup> to R<sup>4</sup> each independently represent an alkyl group having 1 to 20 carbon atoms or a substituted or unsubstituted aryl group having 6 to 30 carbon atoms; in one or both of a pair of groups represented by R<sup>1</sup> and R<sup>2</sup> and a pair of groups represented by R<sup>3</sup> and R<sup>4</sup>, the groups forming the pair may be bonded through -O- or -S-; R<sup>5</sup> to R<sup>16</sup> represents hydrogen

atom, a linear, branched or cyclic alkyl group having 1 to 20 carbon atoms, a linear, branched or cyclic alkoxy group having 1 to 20 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon groups, a substituted or unsubstituted arylamino group having 6 to 30 carbon atoms, a substituted or unsubstituted alkylamino group having 1 to 30 carbon atoms, a substituted or unsubstituted arylalkylamino group having 7 to 30 carbon atoms or a substituted or unsubstituted alkenyl groups having 8 to 30 carbon atoms; a pair of adjacent groups represented by R<sup>5</sup> to R<sup>16</sup> and a pair of adjacent substituents to groups represented by R<sup>5</sup> to R<sup>16</sup> may form a cyclic structure in combination; and at least one of substituents represented by R<sup>5</sup> to R<sup>16</sup> comprises an amine group or an alkenyl group.

## ABSTRACT

An organic electroluminescence device which exhibits an excellent purity of color and a high efficiency of light emission, has a long life and emits reddish light and a novel compound having these characteristics are provided.

The organic electroluminescence device comprises an organic layer disposed between at least one pair of electrodes, wherein the organic layer comprises a compound having a fluoranthene skeleton structure substituted at least with an amine group or an alkenyl group.

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(54) Title: ORGANIC ELECTROLUMINESCENT ELEMENT

(54) 発明の名称: 有機エレクトロルミネッセンス素子

(57) Abstract: An organic electroluminescent element which has a high color purity, high luminescent efficiency, and long life and emits a red color; and a novel compound. The organic electroluminescent element comprises at least one pair of electrodes and an organic layer interposed therebetween, and is characterized in that the organic layer contains a compound comprising a fluoranthene-containing skeleton which has been substituted at least by an amine or alkenyl group.

(57) 要約:

色純度及び発光効率が高く、寿命が長く、赤色系に発光する有機エレクトロルミネッセンス素子及び新規化合物を提供する。

少なくとも一対の電極間に有機層が設けられた有機エレクトロルミネッセンス素子であって、該有機層に、含フルオランテン骨格に少なくともアミン又はアルケニル基が置換されている化合物を含有することを特徴とする有機エレクトロルミネッセンス素子である。

WO 01/23497 A1

## 明 細 書

### 有機エレクトロルミネッセンス素子

#### 技術分野

本発明は壁掛けテレビの平面発光体やディスプレイのバックライト等の光源として使用され、色純度及び発光効率が高く、寿命が長く、赤色系に発光する有機エレクトロルミネッセンス素子及び新規化合物に関するものである。

#### 背景技術

有機物質を使用した有機エレクトロルミネッセンス（EL）素子は、固体発光型の安価な大面積フルカラー表示素子としての用途が有望視され、多くの開発が行われている。一般にEL素子は、発光層および該層をはさんだ一対の対向電極から構成されている。発光は、両電極間に電界が印加されると、陰極側から電子が注入され、陽極側から正孔が注入される。さらに、この電子が発光層において正孔と再結合し、励起状態を生成し、励起状態が基底状態に戻る際にエネルギーを光として放出する現象である。

最近では、有機EL素子ディスプレイの実用化が開始されているものの、フルカラー表示素子は開発途中である。特に、色純度及び発光効率が高く、寿命が長く、赤色系に発光する有機EL素子用発光材料が求められている。

これらを解決しようとするものとして、例えば特開平8-311442号公報には、ナフタセン又はペンタセン誘導体を発光層に添加した赤色発光素子が開示されている。この発光素子は、赤色純度は優れているものの、発光効率が0.7 lm/Wと低く、平均寿命も150 hr未満と不十分であった。平均寿命は、実用化するためには、最低数千hr必要である。また、特開平3-162481号公報には、ジシアノメチレン（DCM）系化合物を発光層に添加した素子も開示

されているが赤色の純度が不十分であった。さらに、特開平10-340782号公報や特開平11-40360号公報などには、フルオランテン系化合物を含有する有機EL素子が開示されている。しかしながら、同公報に開示された化合物を用いた素子が黄色～赤色系に発光せず、発光効率も4cd/A以下と不十分であった。

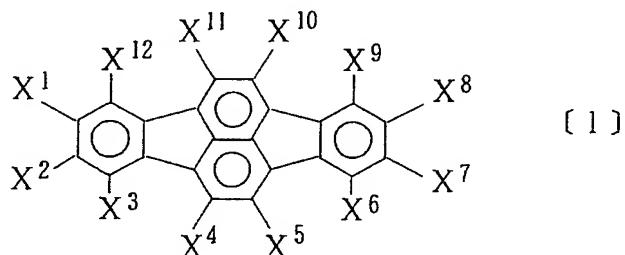
### 発明の開示

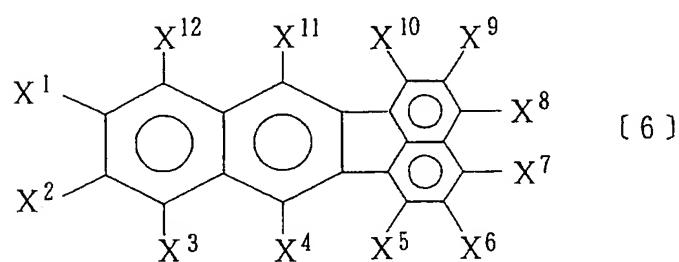
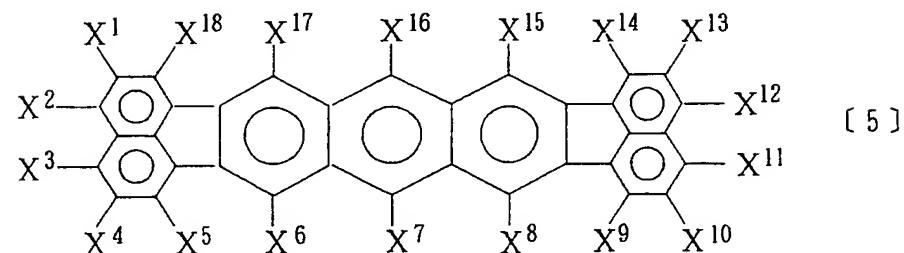
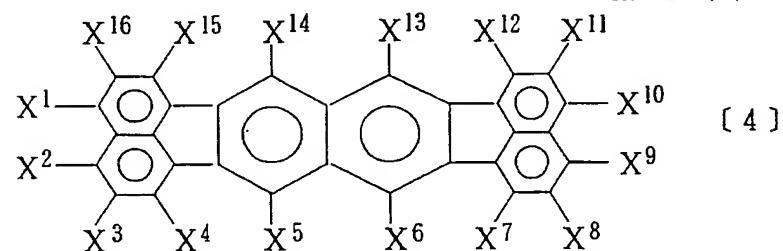
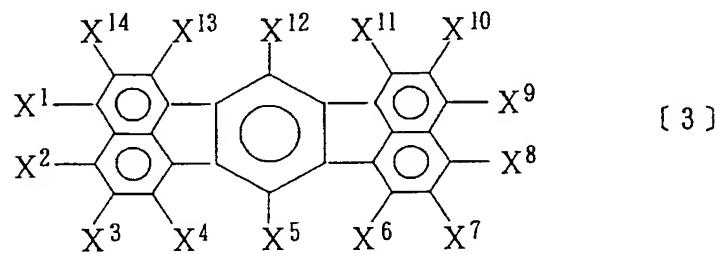
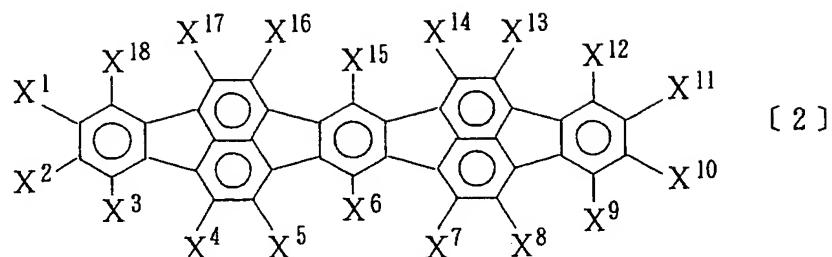
本発明は、前記の課題を解決するためになされたもので、色純度及び発光効率が高く、寿命が長く、赤色系に発光する有機エレクトロルミネッセンス素子及び新規化合物を提供することを目的とするものである。

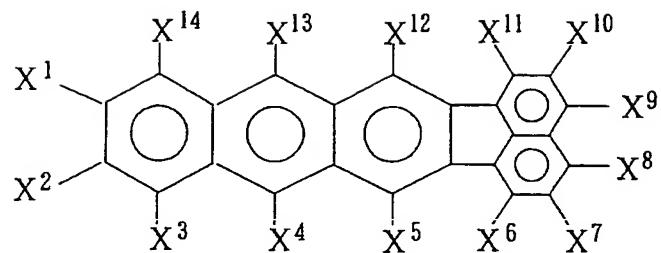
本発明者らは、前記の好ましい性質を有する有機エレクトロルミネッセンス素子（以下、有機EL素子）を開発すべく銳意研究を重ねた結果、含フルオランテン骨格に少なくともアミン又はアルケニル基が置換されている化合物を発光材料として利用することによりその目的を達成し得ることを見出した。

すなわち、本発明の有機EL素子は、少なくとも一対の電極間に有機層が設けられた有機エレクトロルミネッセンス素子であって、該有機層に、含フルオランテン骨格に少なくともアミン又はアルケニル基が置換されている化合物を含有する。

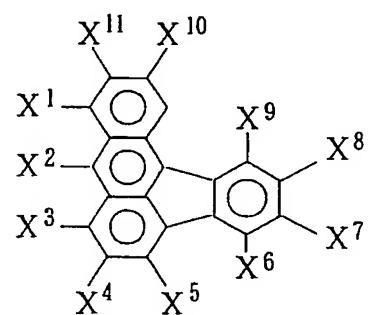
前記化合物は、下記一般式〔1〕～〔18〕のいずれかで示される化合物であることが好ましい。



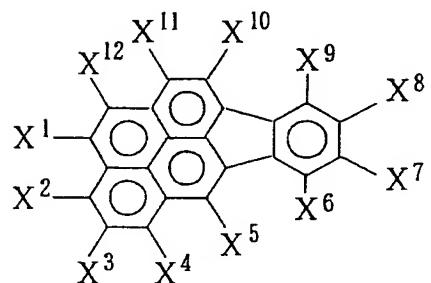




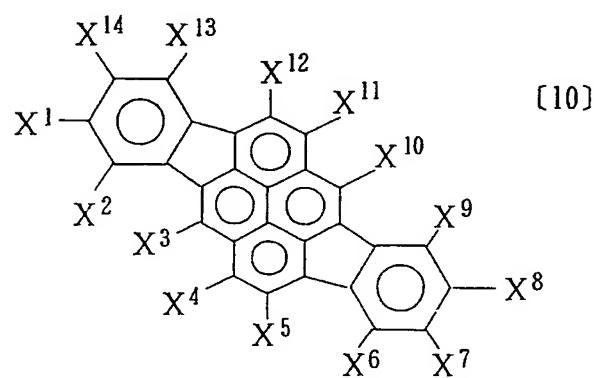
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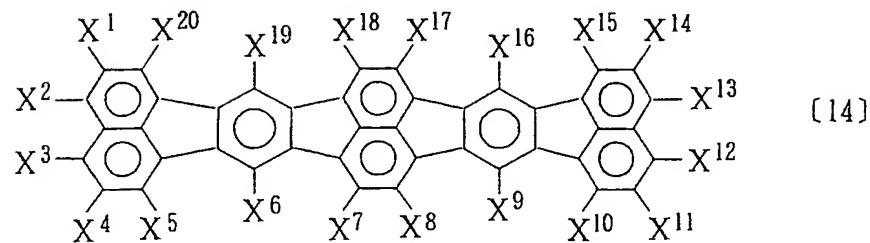
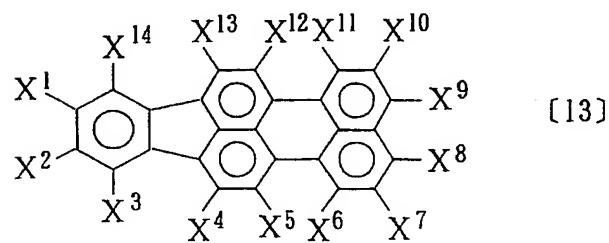
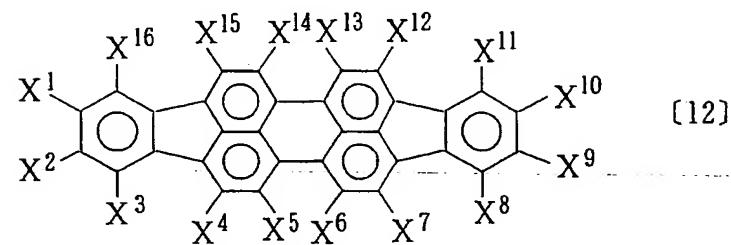
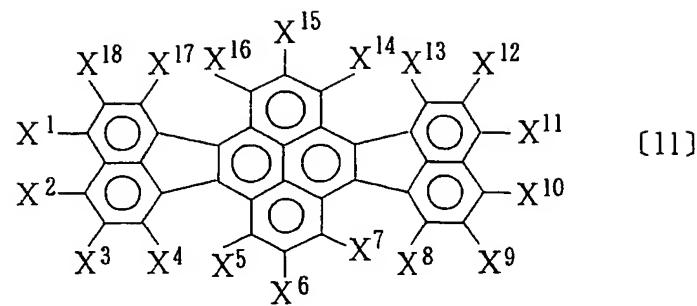
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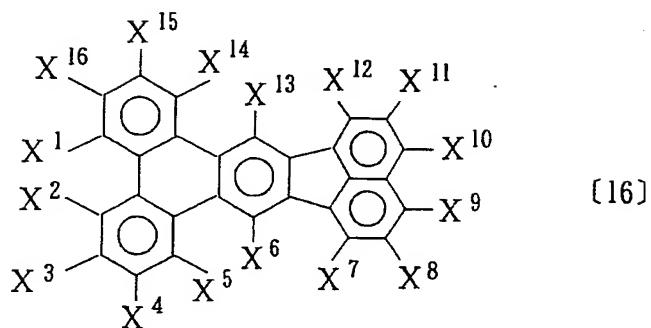
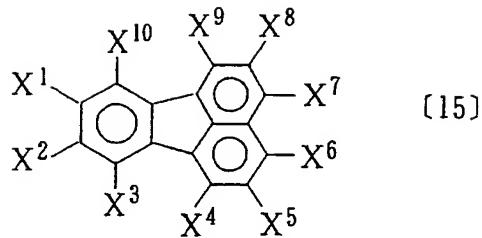


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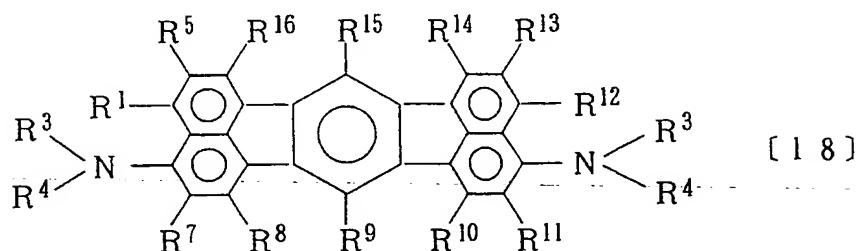
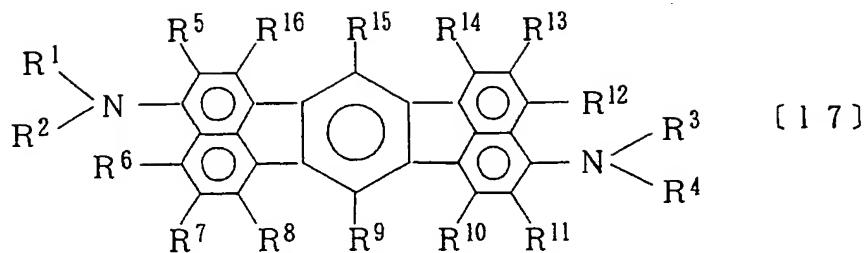


[ 10 ]





[一般式〔1〕～〔16〕式中、 $X^1 \sim X^{20}$ は、それぞれ独立に、水素原子、直鎖、分岐もしくは環状の炭素原子数1～20のアルキル基、直鎖、分岐もしくは環状の炭素原子数1～20のアルコキシ基、置換もしくは無置換の炭素原子数6～30のアリール基、置換もしくは無置換の炭素原子数6～30のアリールオキシ基、置換もしくは無置換の炭素原子数6～30のアリールアミノ基、置換もしくは無置換の炭素原子数1～30のアルキルアミノ基、置換もしくは無置換の炭素原子数7～30のアリールアルキルアミノ基又は置換もしくは無置換炭素原子数8～30のアルケニル基であり、隣接する置換基及び $X^1 \sim X^{20}$ は結合して環状構造を形成してもよい。隣接する置換基がアリール基の時は、置換基は同一であってもよい。ただし、各式中の置換基 $X^1 \sim X^i$  ( $i = 12 \sim 20$ ) の少なくとも一つはアミン又はアルケニル基を含有する。]



[一般式〔17〕～〔18〕式中、R<sup>1</sup>～R<sup>4</sup>は、それぞれ独立に、炭素原子数1～20のアルキル基、置換もしくは無置換の炭素原子数6～30のアリール基であり、R<sup>1</sup>とR<sup>2</sup>及び／又はR<sup>3</sup>とR<sup>4</sup>は、炭素－炭素結合又は－O－、－S－を介して結合していてよい。R<sup>5</sup>～R<sup>16</sup>は、水素原子、直鎖、分岐もしくは環状の炭素原子数1～20のアルキル基、直鎖、分岐もしくは環状の炭素原子数1～20のアルコキシ基、置換もしくは無置換の炭素原子数6～30のアリール基、置換もしくは無置換の炭素原子数6～30のアリールオキシ基、置換もしくは無置換の炭素原子数6～30のアリールアミノ基、置換もしくは無置換の炭素原子数1～30のアルキルアミノ基、置換もしくは無置換の炭素原子数7～30のアリールアルキルアミノ基又は置換もしくは無置換炭素原子数8～30のアルケニル基であり、隣接する置換基及びR<sup>5</sup>～R<sup>16</sup>は結合して環状構造を形成していてよい。ただし、各式中の置換基R<sup>5</sup>～R<sup>16</sup>の少なくとも一つはアミン又はアルケニル基を含有する。]

また、本発明の新規化合物は、上記一般式〔1〕～〔18〕のいずれかで表される化合物である。

#### 図面の簡単な説明

図1 本発明の新規化合物の一例の<sup>1</sup>H-NMRスペクトルを示す図である。

図2 本発明の新規化合物の別の例の<sup>1</sup>H-NMRスペクトルを示す図である。

図3 本発明の新規化合物の別の例の<sup>1</sup>H-NMRスペクトルを示す図である。

#### 発明を実施するための最良の形態

本発明の有機EL素子は、少なくとも一対の電極間に有機層が設けられた有機エレクトロルミネッセンス素子であって、該有機層に、含フルオランテン骨格に少なくともアミン又はアルケニル基が置換されている化合物を含有する。

この化合物は、新規化合物であり、上記一般式〔1〕～〔18〕のいずれかで示される化合物である。

一般式〔1〕～〔16〕式中、X<sup>1</sup>～X<sup>20</sup>は、それぞれ独立に、水素原子、直鎖、分岐もしくは環状の炭素原子数1～20のアルキル基、直鎖、分岐もしくは環状の炭素原子数1～20のアルコキシ基、置換もしくは無置換の炭素原子数6～30のアリール基、置換もしくは無置換の炭素原子数6～30のアリールオキシ基、置換もしくは無置換の炭素原子数6～30のアリールアミノ基、置換もしくは無置換の炭素原子数1～30のアルキルアミノ基、置換もしくは無置換の炭素原子数7～30のアリールアルキルアミノ基又は置換もしくは無置換炭素原子数8～30のアルケニル基であり、隣接する置換基及びX<sup>1</sup>～X<sup>20</sup>は結合して環状構造を形成していてもよい。隣接する置換基がアリール基の時は、置換基は同一であってもよい。ただし、各式中の置換基X<sup>i</sup>～X<sup>i</sup>（i=12～20）の少なくとも一つはアミン又はアルケニル基を含有する。ここで、隣接する置換基がアリール基であり、同一である場合には、隣接する結合手が2価の芳香環基に結

合することを意味する。

一般式〔17〕～〔18〕式中、R<sup>1</sup>～R<sup>4</sup>は、それぞれ独立に、炭素原子数1～20のアルキル基、置換もしくは無置換の炭素原子数6～30のアリール基であり、R<sup>1</sup>とR<sup>2</sup>及び／又はR<sup>3</sup>とR<sup>4</sup>は、炭素-炭素結合又は-O-, -S-を介して結合していてもよい。R<sup>5</sup>～R<sup>16</sup>は、水素原子、直鎖、分岐もしくは環状の炭素原子数1～20のアルキル基、直鎖、分岐もしくは環状の炭素原子数1～20のアルコキシ基、置換もしくは無置換の炭素原子数6～30のアリール基、置換もしくは無置換の炭素原子数6～30のアリールオキシ基、置換もしくは無置換の炭素原子数6～30のアリールアミノ基、置換もしくは無置換の炭素原子数1～30のアルキルアミノ基、置換もしくは無置換の炭素原子数7～30のアリールアルキルアミノ基又は置換もしくは無置換炭素原子数8～30のアルケニル基であり、隣接する置換基及びR<sup>5</sup>～R<sup>16</sup>は結合して環状構造を形成していてもよい。ただし、各式中の置換基R<sup>5</sup>～R<sup>16</sup>の少なくとも一つはアミン又はアルケニル基を含有する。

ここで、上記一般式〔1〕～〔18〕の化合物において好ましい化合物を以下に示す。

含フルオランテン骨格が、少なくとも5つ以上の縮合環よりなることが好ましく、さらに好ましくは6つ以上の縮合環よりなることである。このような化合物を用いることにより、より長波長の黄色～赤色系の発光が可能である。

含フルオランテン骨格が、アミノ基で置換されていることが好ましい。このような化合物を用いることにより、より長寿命の発光材料が得られる。

このアミノ基は、置換もしくは無置換のアリールアミノ基であることが好ましく、さらに好ましくはジアリールアミノ基である。このような化合物を用いることにより、前記化合物を発光層中に2重量%以上の高い濃度で添加しても、濃度消光しにくく、高い効率の素子を得ることができる。

前記化合物は、線対称、回転対称などの対称性を有していることが好ましい。

このような化合物を用いることにより、素子の耐久性が向上するとともに、蛍光量子効率が高くなる。

前記化合物は、10個以上の六員環又は五員環構造を有することが好ましい。このようにすることで、ガラス転移温度が100°C以上となり、この化合物よりなる層又は添加された層の熱安定性が高まる。

前記化合物は、炭素原子数4以上のアリール基、環状アルキル基、アリールオキシ基、アリールチオ基、アリールアルキル基等が含まれることが好ましい。これらの基は、立耐障害性があるため、濃度消光を防ぐ作用がある。

一般式〔17〕又は〔18〕においては、R<sup>15</sup>及びR<sup>9</sup>が置換基を有する基であることが好ましい。このようにすることで、化合物の酸化、還元に対する安定性が高まり、素子が長寿命となる。

含フルオランテン骨格が、アミノ基で2置換されている化合物、アルケニル基が2置換されている化合物及びアミノ基とアルケニル基とで置換されている化合物は異性体が存在する。

一例として、含フルオランテン骨格が、7, 14-ジフェニルアセナフト〔1, 2-k〕フルオランテンの場合について説明する。

アセナフト〔1, 2-k〕フルオランテンのジブロモ体は、3, 10-ジブロモ-7, 14-ジフェニルアセナフト〔1, 2-k〕フルオランテン（A体）と3, 11-ジブロモ-7, 14-ジフェニルアセナフト〔1, 2-k〕フルオランテン（B体）の2種の異性体が存在する。

これら、A体、B体の中間体より得られる最終生成物としては、A体由来のアミノ置換体とB体由来のアミノ置換体が存在する。また、この最終生成物を得る際、（1）ジブロモ体が溶存する反応液の可溶部よりジブロモ体を得るか、（2）前記反応液の可溶部より得た生成物を再度溶媒に溶解した後、再結晶後、析出物よりジブロモ体を得るか、（3）（2）の再結晶後の溶媒中よりジブロモ体を得ることにより、A体、B体の異性体比が異なる。これらの処理方法、処理時に

用いる溶媒種を選択することにより、A体：B体=10：90～90：10の各種の異性体比（モル比）を持つ目的物を得ることができる。

また、異性対比の誤差の範囲が、①A体：B体=x±10:y±10 (x+y=100)であることが好ましく、特に好ましくは②A体：B体=x±5:y±5 (x+y=100)である。このような①の場合、異性体比がほぼ一定、②の場合、異性体比が一定と言うことにする。

本発明の前記化合物が異性体を有するときは、複数の異性体を有機層に含有させることができる。好ましくは、異性体をほぼ一定又は一定とし、素子を製造することができる。このようにすることで、素子から放出される発光スペクトルを一定とすることができます。すなわち、発光色を一定とすることができます、さらに異性体比を変えることにより、発光色を変えることができる。また、当然、異性体を排除する場合には、単一の化合物のみを有機層に含有させることも可能である。

また、このような異性体においては、一方の異性体が他方より長波長を発光することができる。このため、好ましくは長波長を発光しうる異性体と該異性体より短波長を発光しうる異性体とのモル比が、90：10～60：40であり、さらに好ましくは99：1～70：30とすることにより、より長波長の発光、例えば赤色発光が可能となる。

なお、異性体比は<sup>1</sup>H-NMRを用い異性体ごとにNMRピークのケミカルシフトが異なることを利用し、各々の異性体に帰属するピークシグナルの面積比で算出することができる。

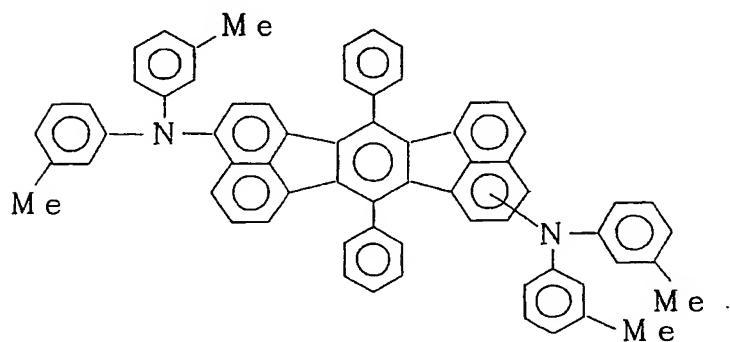
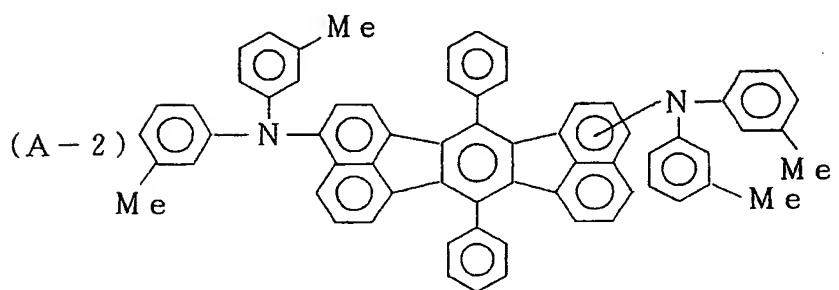
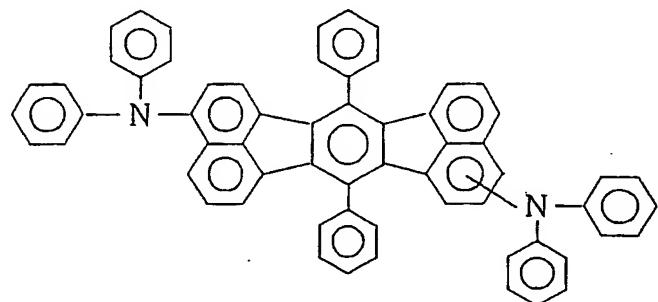
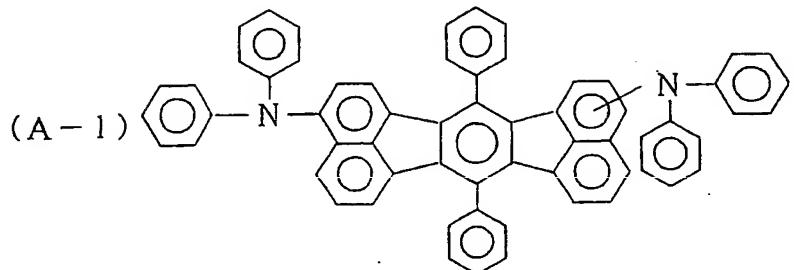
前記有機層が、正孔輸送層及び／又は発光層であることが好ましい。

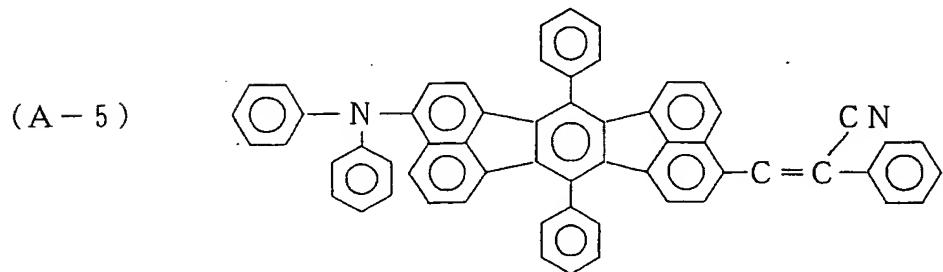
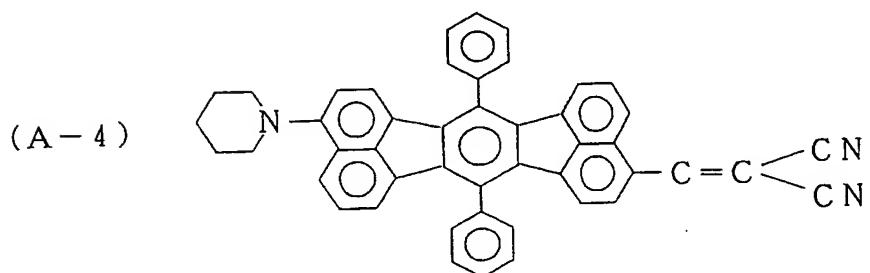
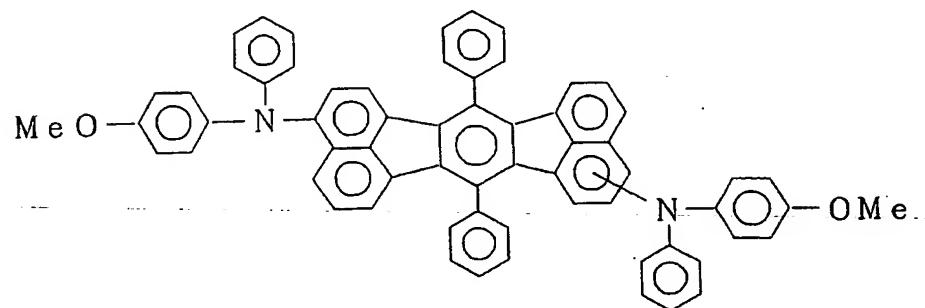
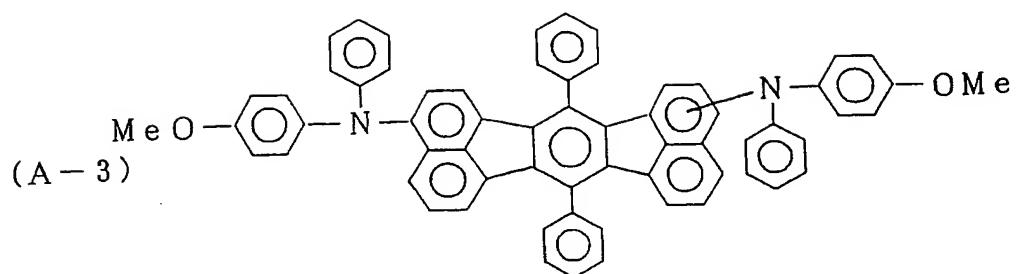
前記有機層と電極との間に無機化合物層を設けていても良い。

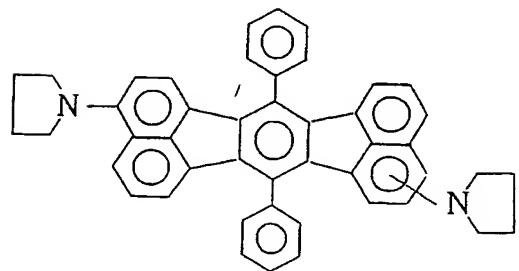
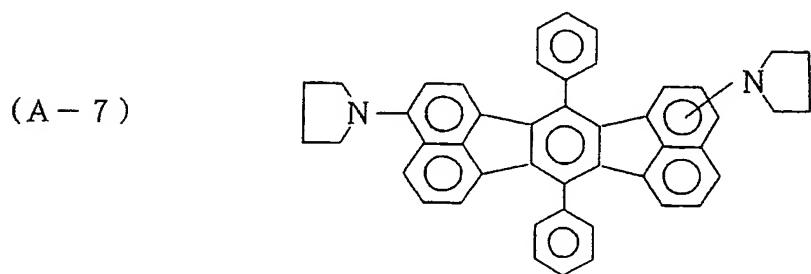
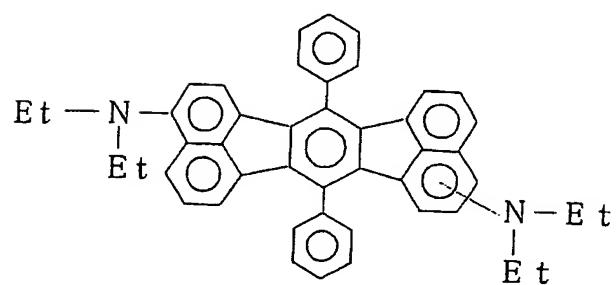
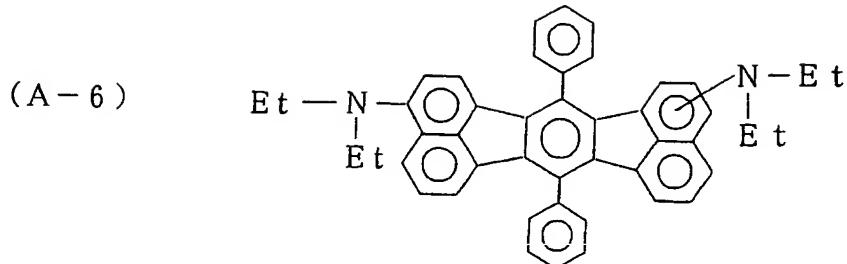
本発明の有機EL素子は、赤色系の発光をするものである。

以下に、本発明の一般式〔1〕～〔18〕の化合物の代表例(A-1)～(A-18)及び(B-1)～(B-17)を例示するが、本発明はこの代表例に限

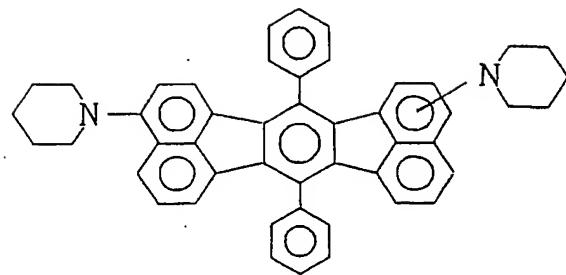
定されるものではない。※Meはメチル基、Etはエチル基を示す。



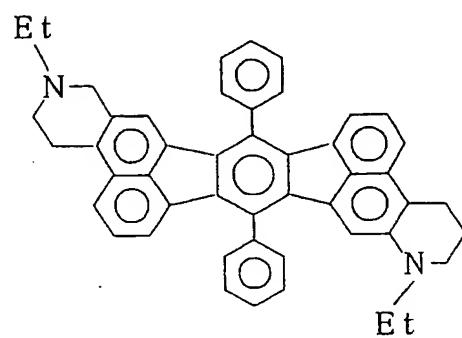




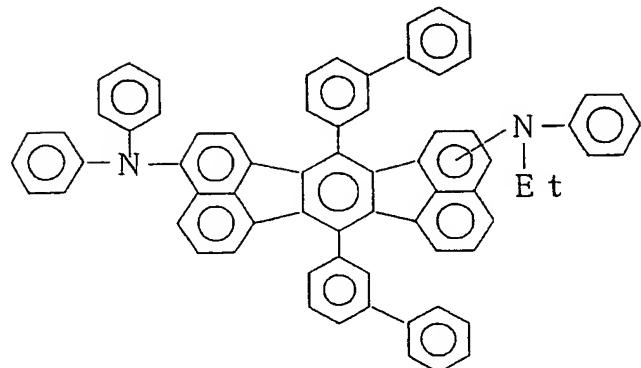
(A - 8 )

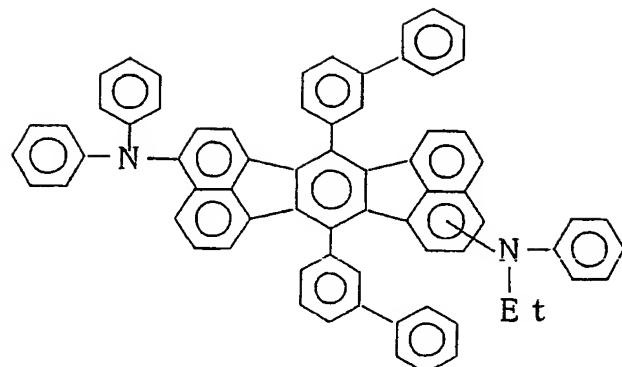


(A - 9 )

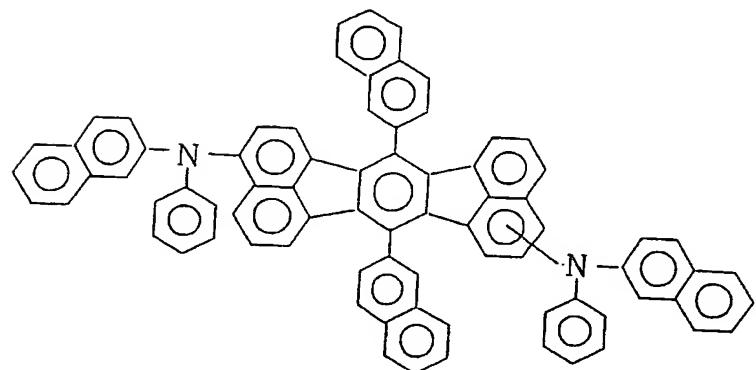
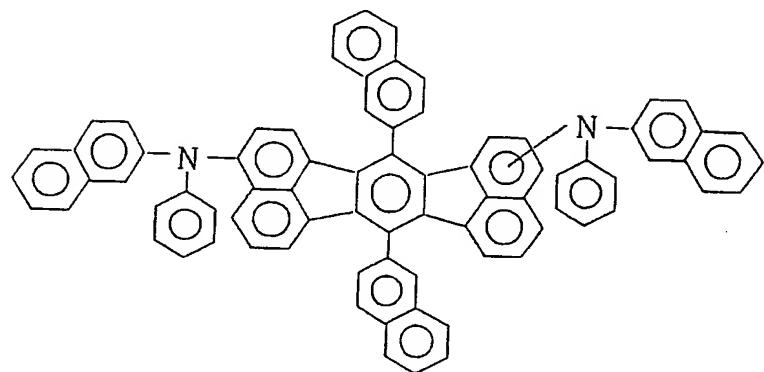


(A - 10)

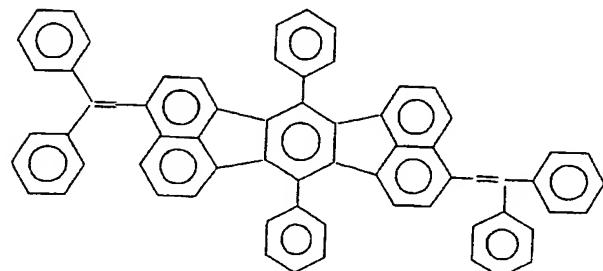


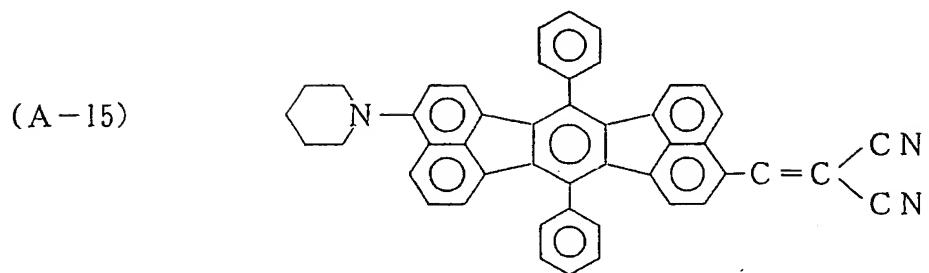
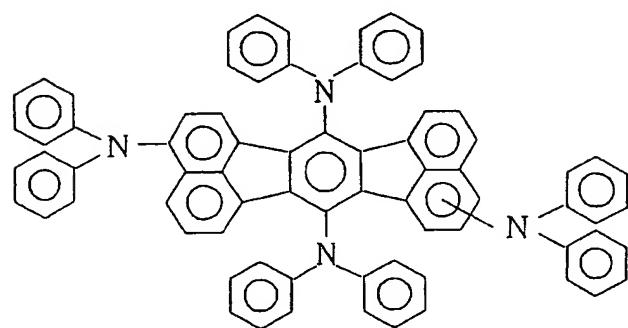
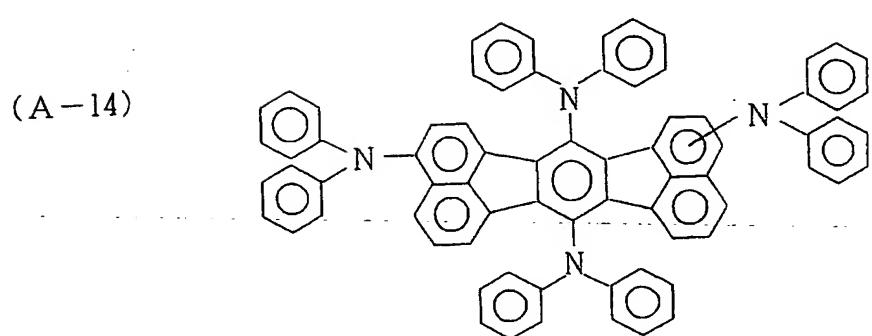
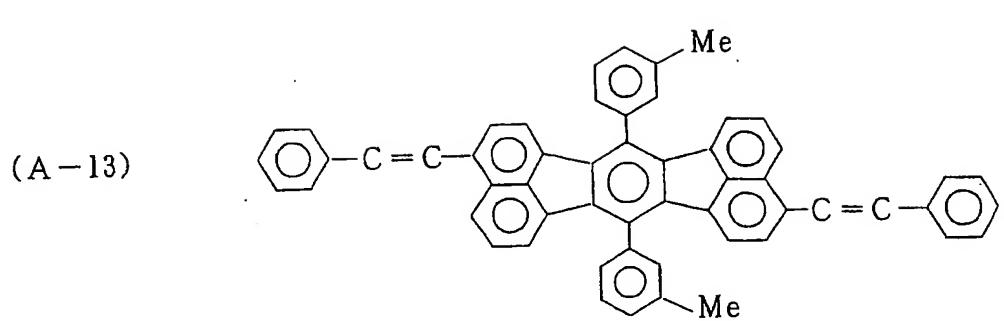


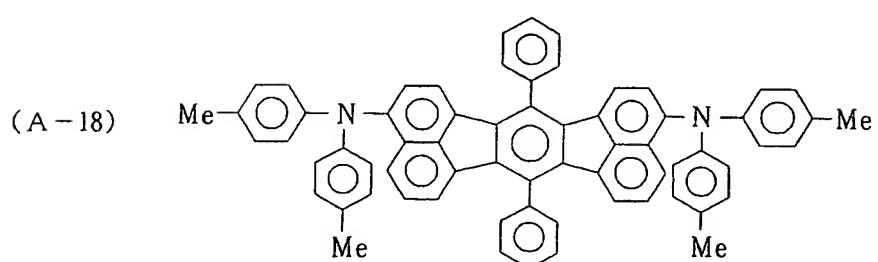
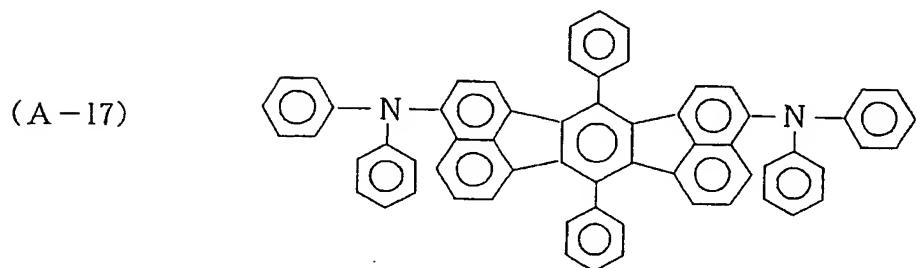
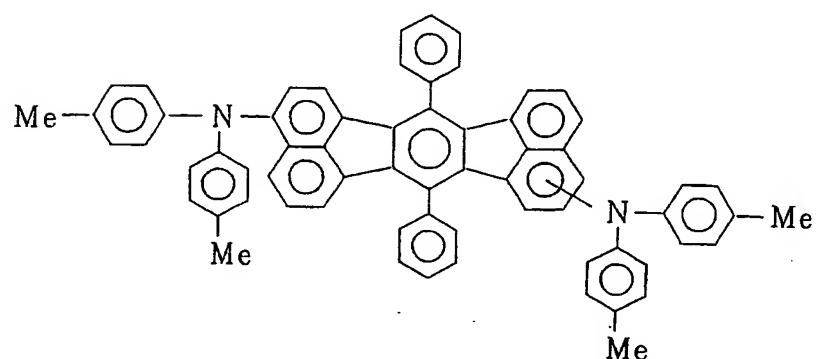
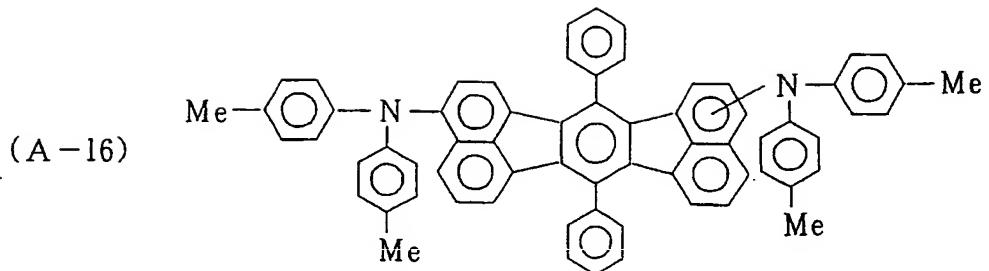
(A-11)

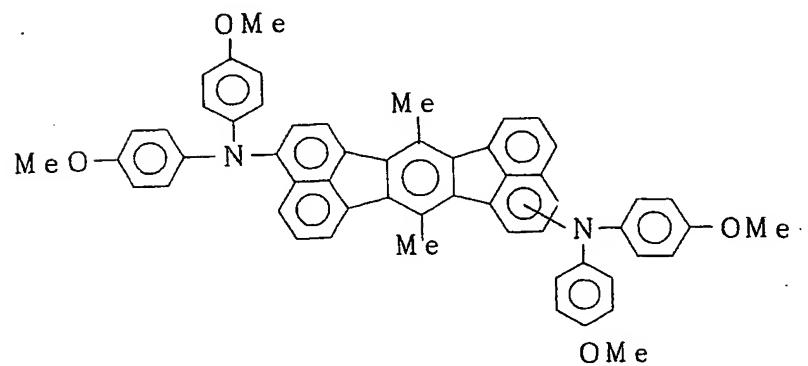
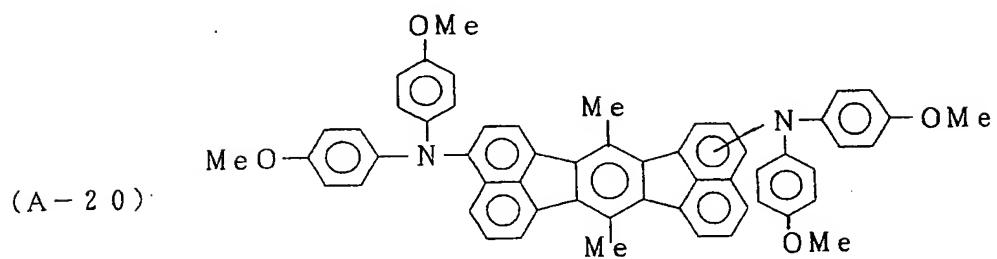
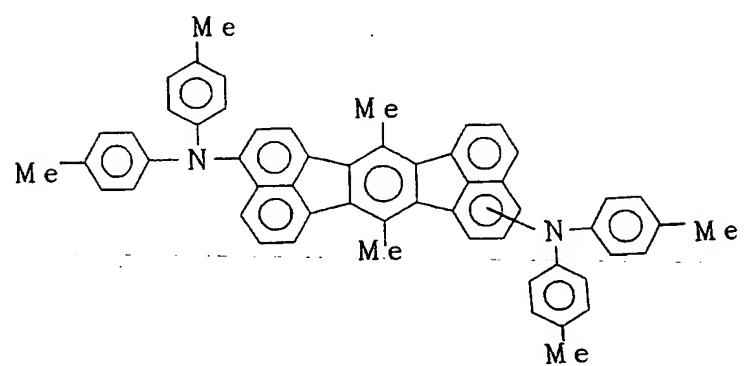
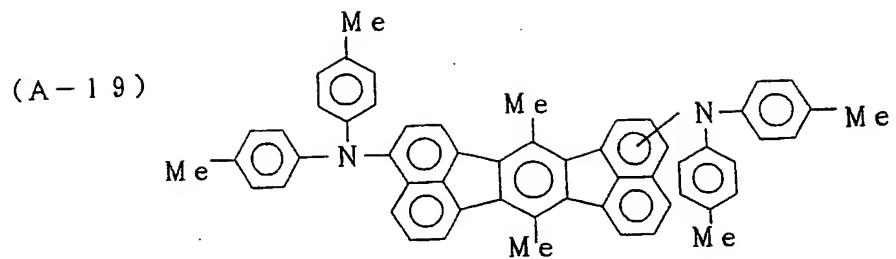


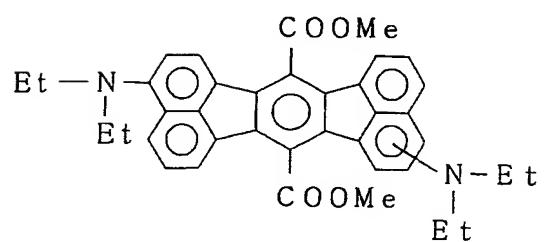
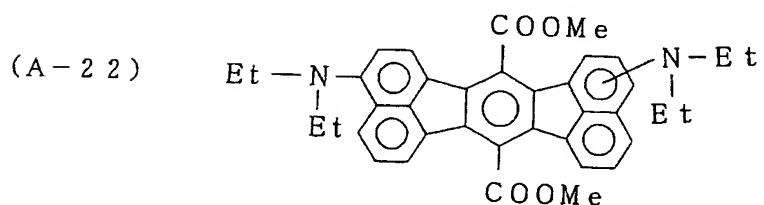
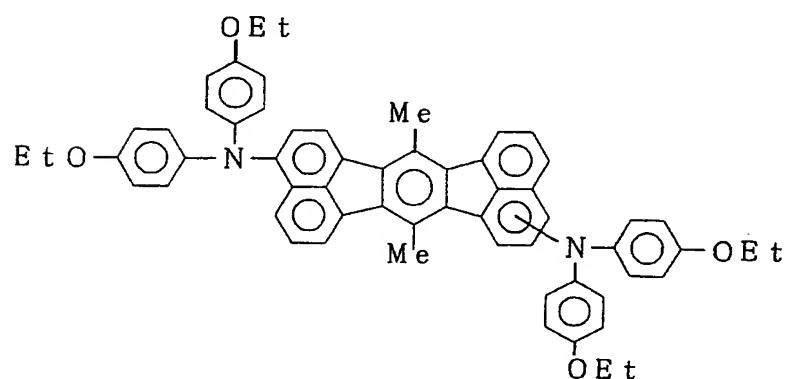
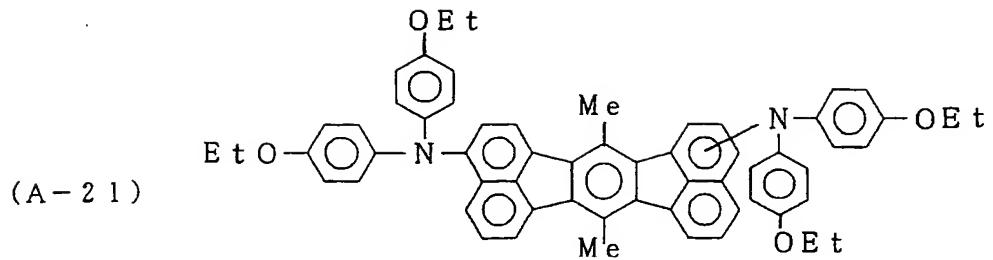
(A-12)



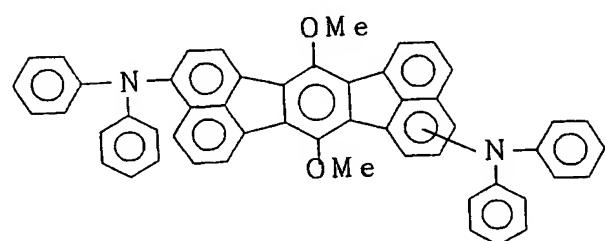
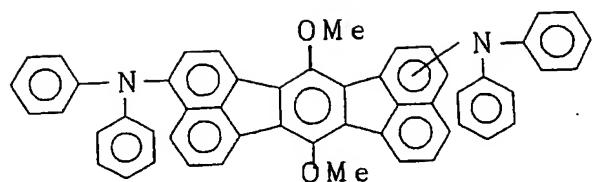




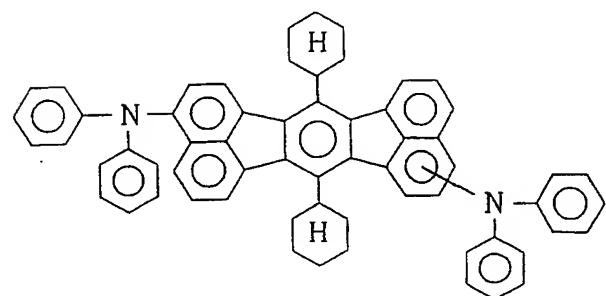
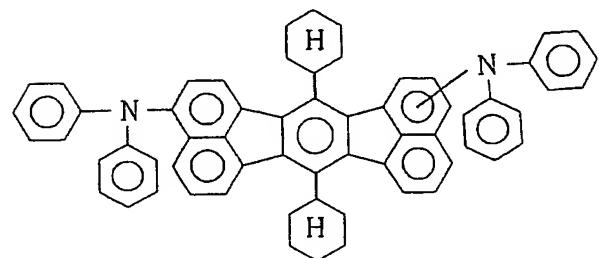


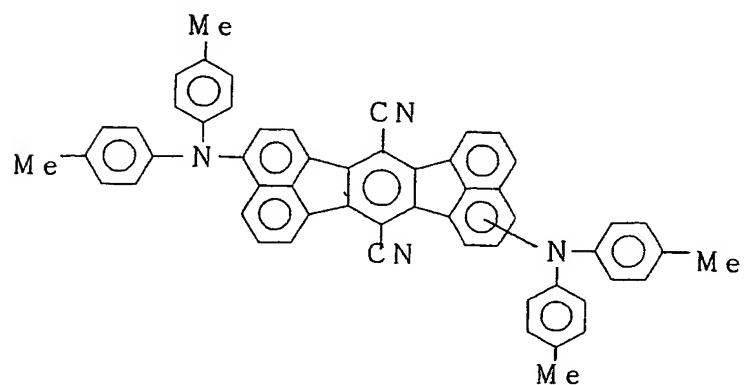
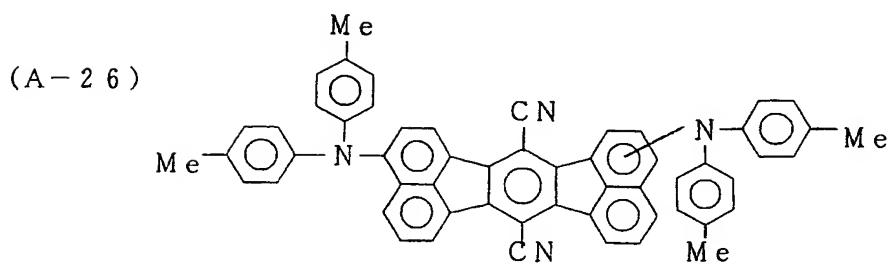
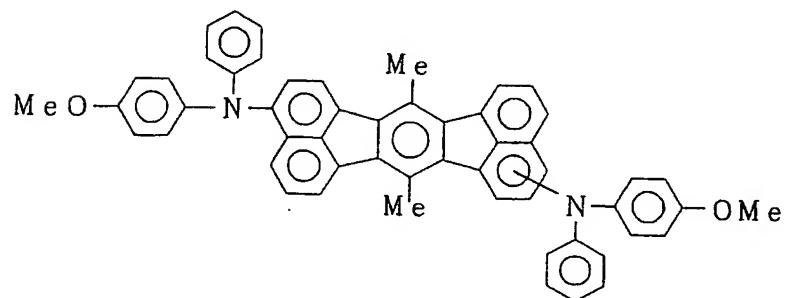
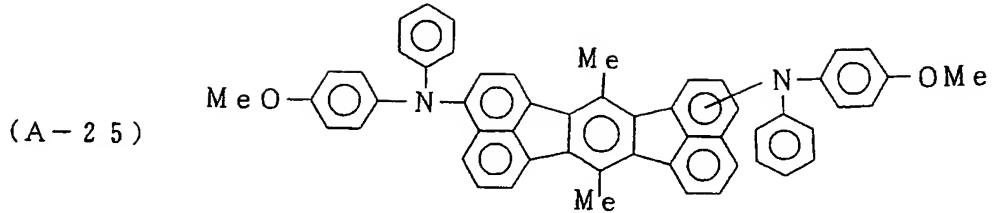


(A - 2 3)

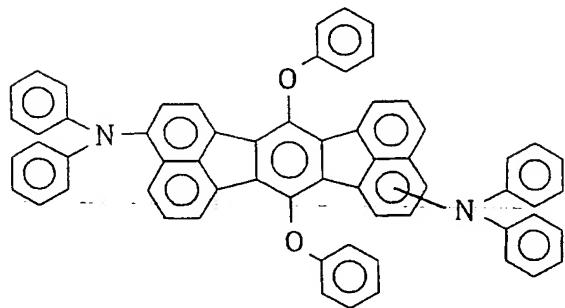
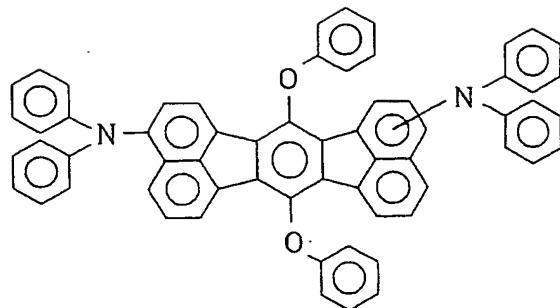


(A - 2 4)

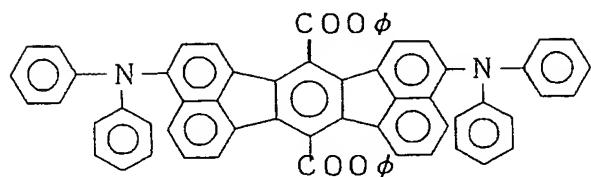




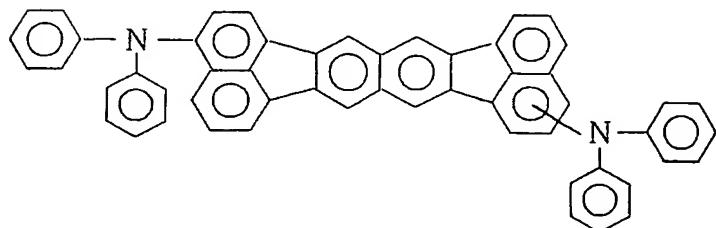
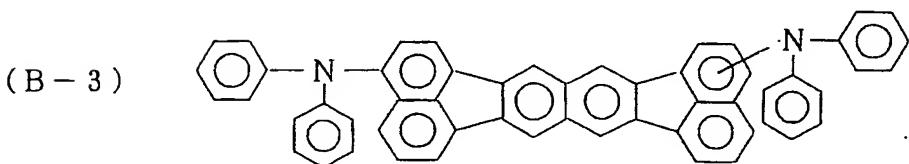
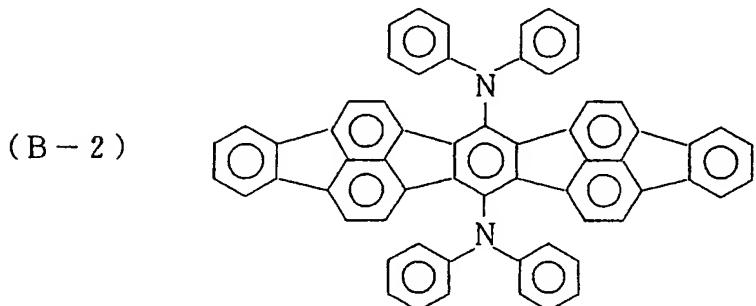
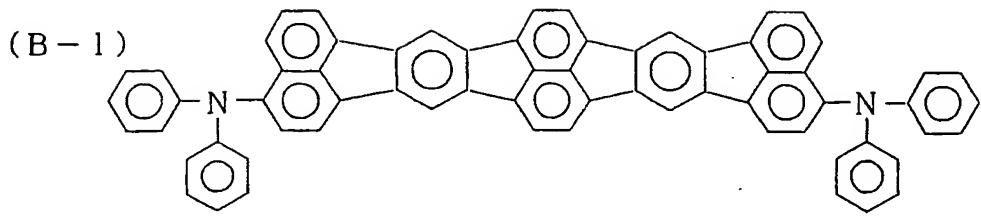
(A-27)

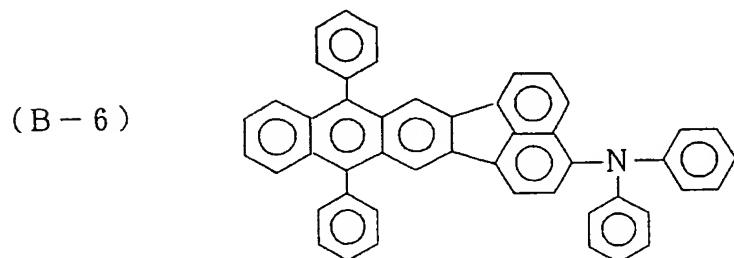
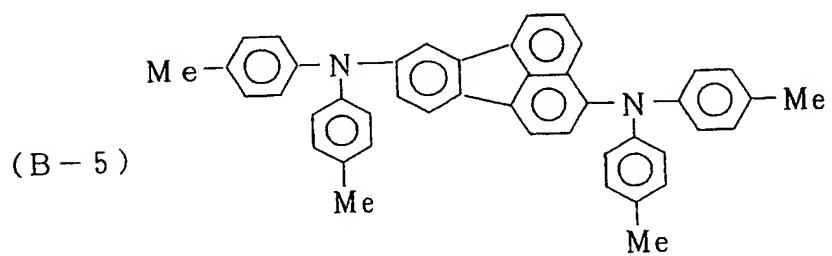
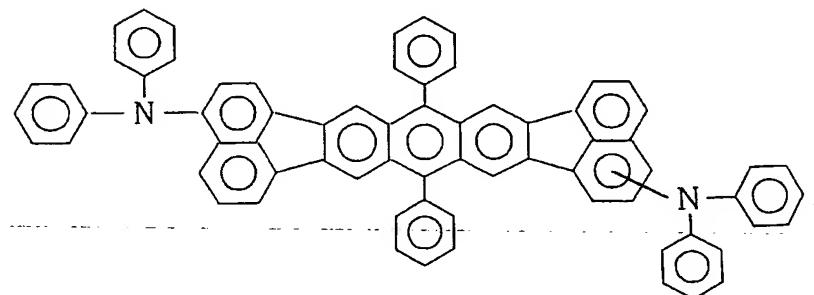
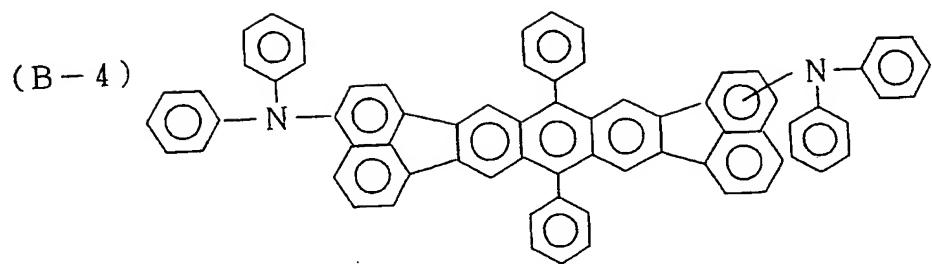


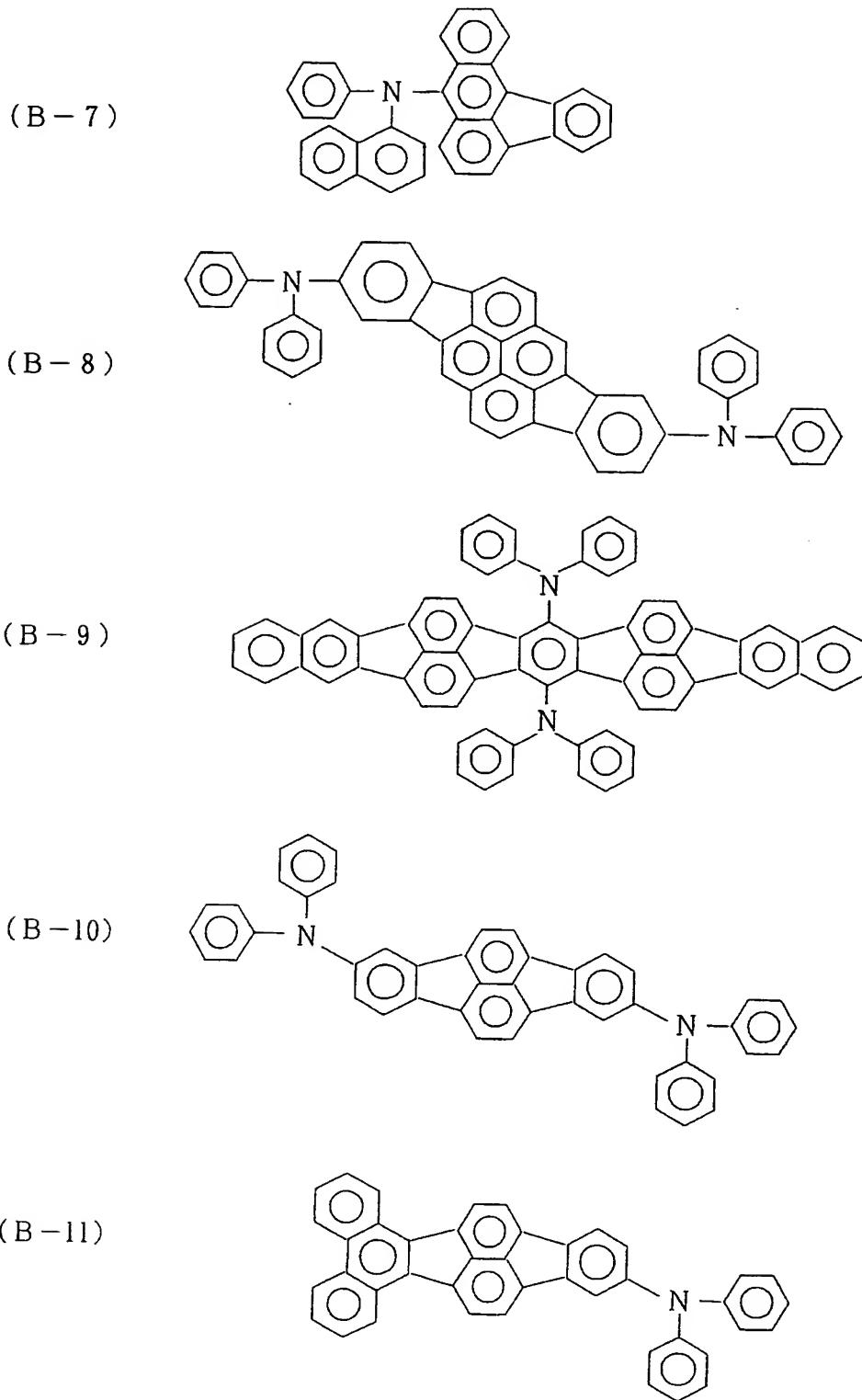
(A-28)



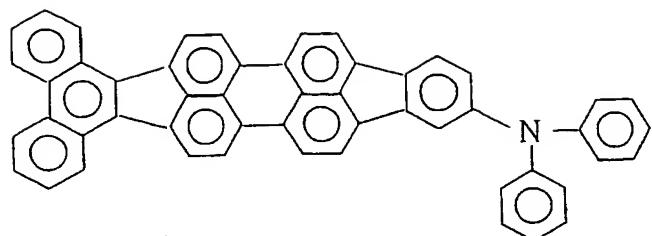
(φはフェニル基)



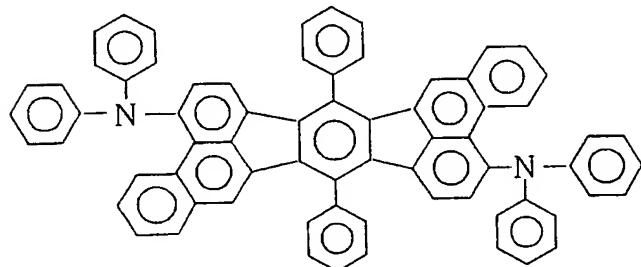




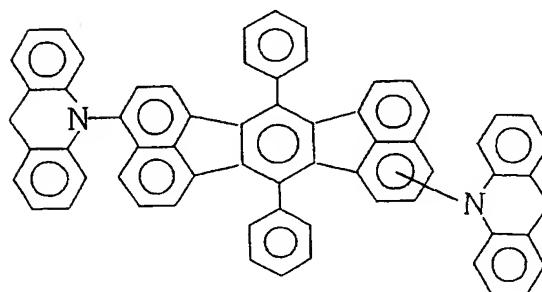
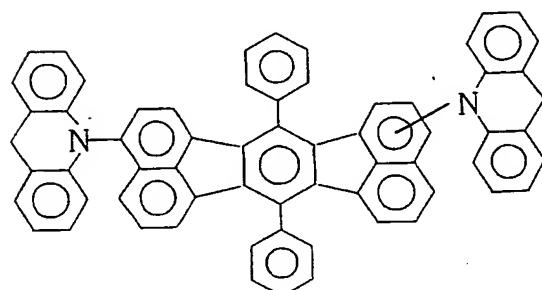
(B - 12)

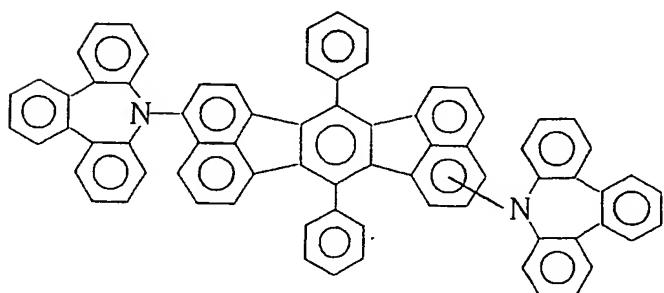
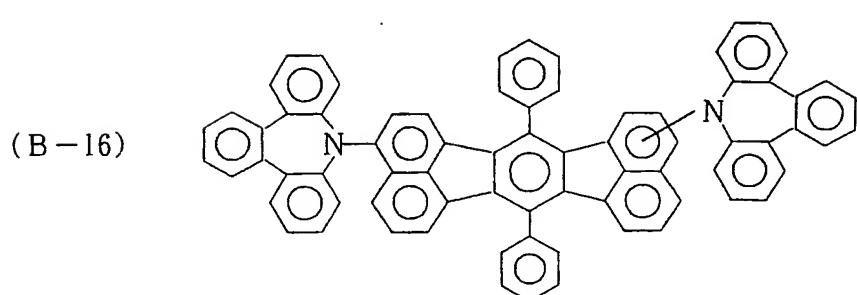
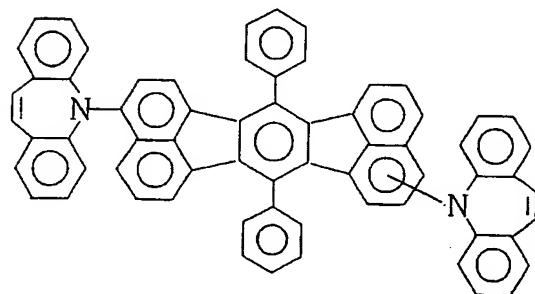
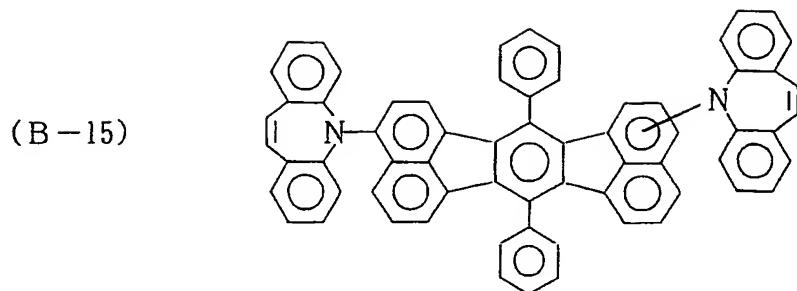


(B - 13)

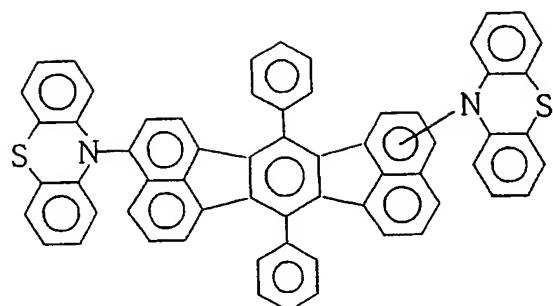


(B - 14)

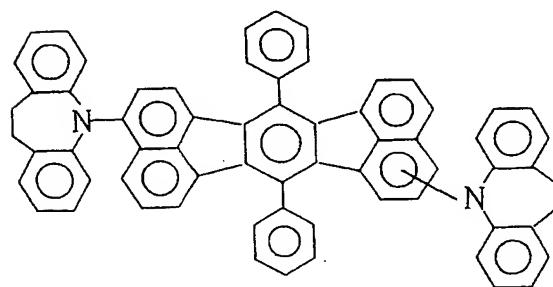
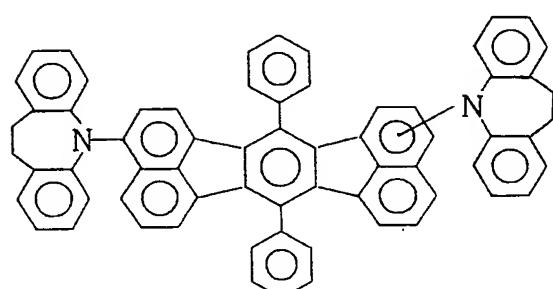


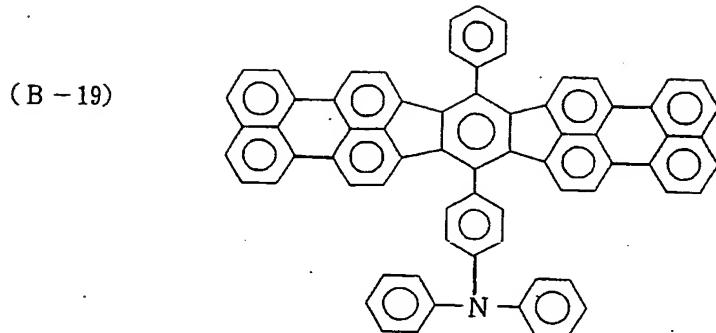


(B - 17)



(B - 18)





本発明の有機EL素子に使用する化合物は、含フルオランテン骨格にアミン基又はアルケニル基が置換されているため、蛍光収率が高く、赤色系又は黄色系の発光をする。このため、この化合物を用いた有機EL素子は、赤色系～黄色系に発光し、高発光効率で長寿命である。

本発明の有機EL素子は、陽極と陰極間に一層もしくは多層の有機層を形成した素子である。一層型の場合、陽極と陰極との間に発光層を設けている。発光層は、発光材料を含有し、それに加えて陽極から注入した正孔、もしくは陰極から注入した電子を発光材料まで輸送させるために、正孔注入材料もしくは電子注入材料を含有しても良い。しかしながら、発光材料は、極めて高い蛍光量子効率、高い正孔輸送能力および電子輸送能力を併せ持ち、均一な薄膜を形成することが好ましい。多層型の有機EL素子は、（陽極／正孔注入層／発光層／陰極）、（陽極／発光層／電子注入層／陰極）、（陽極／正孔注入層／発光層／電子注入層／陰極）の多層構成で積層したものがある。

発光層には、必要に応じて、本発明の一般式〔1〕～〔18〕の化合物に加えてさらなる公知の発光材料、ドーピング材料、正孔注入材料や電子注入材料を使用することもできる。この化合物の好ましい使用法としては、発光層、電子注入層、正孔輸送層又は正孔注入層のいずれかの層に、濃度1～70重量%で添加する。さらに好ましくは、濃度1～20重量%であり、特に本発明の化合物をドーピング材料として用いることが好ましい。

有機EL素子は、多層構造にすることにより、クエンチングによる輝度や寿命の低下を防ぐことができる。必要があれば、発光材料、他のドーピング材料、正孔注入材料や電子注入材料を組み合わせて使用することができる。また、他のドーピング材料により、発光輝度や発光効率の向上、赤色や白色の発光を得ることもできる。また、正孔注入層、発光層、電子注入層は、それぞれ二層以上の層構成により形成されても良い。その際には、正孔注入層の場合、電極から正孔を注入する層を正孔注入層、正孔注入層から正孔を受け取り発光層まで正孔を輸送する層を正孔輸送層と呼ぶ。同様に、電子注入層の場合、電極から電子を注入する層を電子注入層、電子注入層から電子を受け取り発光層まで電子を輸送する層を電子輸送層と呼ぶ。これらの各層は、材料のエネルギー準位、耐熱性、有機層もしくは金属電極との密着性等の各要因により選択されて使用される。

一般式〔1〕～〔18〕の化合物と共に有機層に使用できる発光材料またはホスト材料としては、アントラセン、ナフタレン、フェナントレン、ピレン、テトラセン、コロネン、クリセン、フルオレセイン、ペリレン、フタロペリレン、ナフタロペリレン、ペリノン、フタロペリノン、ナフタロペリノン、ジフェニルブタジエン、テトラフェニルブタジエン、クマリン、オキサジアゾール、アルダジン、ビスベンゾキサゾリン、ビススチリル、ピラジン、シクロペンタジエン、キノリン金属錯体、アミノキノリン金属錯体、ベンゾキノリン金属錯体、イミン、ジフェニルエチレン、ビニルアントラセン、ジアミノカルバゾール、ピラン、チオピラン、ポリメチン、メロシアニン、イミダゾールキレート化オキシノイド化合物、キナクリドン、ルブレン、スチルベン系誘導体及び蛍光色素等が挙げられるが、これらに限定されるものではない。

正孔注入材料としては、正孔を輸送する能力を持ち、陽極からの正孔注入効果、発光層または発光材料に対して優れた正孔注入効果を有し、発光層で生成した励起子の電子注入層または電子注入材料への移動を防止し、かつ薄膜形成能力の優れた化合物が好ましい。具体的には、フタロシアニン誘導体、ナフタロシアニ

ン誘導体、ポルフィリン誘導体、オキサゾール、オキサジアゾール、トリアゾール、イミダゾール、イミダゾロン、イミダゾールチオン、ピラゾリン、ピラゾロン、テトラヒドロイミダゾール、オキサゾール、オキサジアゾール、ヒドラゾン、アシルヒドラゾン、ポリアリールアルカン、スチルベン、ブタジエン、ベンジジン型トリフェニルアミン、スチリルアミン型トリフェニルアミン、ジアミン型トリフェニルアミン等と、それらの誘導体、およびポリビニルカルバゾール、ボリシラン、導電性高分子等の高分子材料が挙げられるが、これらに限定されるものではない。

本発明の有機EL素子において使用できる正孔注入材料の中で、さらに効果的な正孔注入材料は、芳香族三級アミン誘導体もしくはフタロシアニン誘導体である。

芳香族三級アミン誘導体の具体例は、トリフェニルアミン、トリトリルアミン、トリルジフェニルアミン、N, N'-ジフェニル-N, N'-(3-メチルフェニル)-1, 1'-ビフェニル-4, 4'-ジアミン、N, N, N', N'- (4-メチルフェニル)-1, 1'-フェニル-4, 4'-ジアミン、N, N, N', N'- (4-メチルフェニル)-1, 1'-ビフェニル-4, 4'-ジアミン、N, N, N', N'- (4-メチルフェニル)-1, 1'-ビフェニル-4, 4'-ジアミン、N, N'-ジフェニル-N, N'-ジナフチル-1, 1'-ビフェニル-4, 4'-ジアミン、N, N'- (メチルフェニル)-N, N'- (4-n-ブチルフェニル)-フェナントレン-9, 10-ジアミン、N, N-ビス(4-ジ-4-トリルアミノフェニル)-4-フェニル-シクロヘキサン等、もしくはこれらの芳香族三級アミン骨格を有したオリゴマーもしくはポリマーであるが、これらに限定されるものではない。

フタロシアニン(Pc)誘導体の具体例は、H<sub>2</sub>Pc、CuPc、CoPc、NiPc、ZnPc、PdPc、FePc、MnPc、CIAIPc、ClGaPc、ClInPc、ClSnPc、Cl<sub>2</sub>SiPc、(HO)AlPc、(HO)GaPc、VO<sub>2</sub>Pc、TiOPc、MoOPc、GaPc-O-GaPc等

のフタロシアニン誘導体およびナフタロシアニン誘導体であるが、これらに限定されるものではない。

電子注入材料としては、電子を輸送する能力を持ち、陰極からの電子注入効果、発光層または発光材料に対して優れた電子注入効果を有し、発光層で生成した励起子の正孔注入層への移動を防止し、かつ薄膜形成能力の優れた化合物が好ましい。具体的には、フルオレノン、アントラキノジメタン、ジフェノキノン、チオピランジオキシド、オキサゾール、オキサジアゾール、トリアゾール、イミダゾール、ペリレンテトラカルボン酸、フレオレニリデンメタン、アントラキノジメタン、アントロン等とそれらの誘導体が挙げられるが、これらに限定されるものではない。また、正孔注入材料に電子受容物質を、電子注入材料に電子供与性物質を添加することにより電荷注入性を向上させることもできる。

本発明の有機EL素子において、さらに効果的な電子注入材料は、金属錯体化合物もしくは含窒素五員環誘導体である。

金属錯体化合物の具体例は、8-ヒドロキシキノリナートリチウム、ビス(8-ヒドロキシキノリナート)亜鉛、ビス(8-ヒドロキシキノリナート)銅、ビス(8-ヒドロキシキノリナート)マンガン、トリス(8-ヒドロキシキノリナート)アルミニウム、トリス(2-メチル-8-ヒドロキシキノリナート)ガリウム、ビス(10-ヒドロキシベンゾ[h]キノリナート)ベリリウム、ビス(10-ヒドロキシベンゾ[h]キノリナート)亜鉛、ビス(2-メチル-8-キノリナート)クロロガリウム、ビス(2-メチル-8-キノリナート)(o-クレゾラート)ガリウム、ビス(2-メチル-8-キノリナート)(1-ナフトラート)アルミニウム、ビス(2-メチル-8-キノリナート)(2-ナフトラート)ガリウム等が挙げられるが、これらに限定されるものではない。

また、含窒素五員誘導体は、オキサゾール、チアゾール、オキサジアゾール、チアジアゾールもしくはトリアゾール誘導体が好ましい。具体的には、2, 5-

ビス(1-フェニル)-1,3,4-オキサゾール、ジメチルPOPPOP、2,5-ビス(1-フェニル)-1,3,4-チアゾール、2,5-ビス(1-フェニル)-1,3,4-オキサジアゾール、2-(4'-tert-ブチルフェニル)-5-(4"-ビフェニル)-1,3,4-オキサジアゾール、2,5-ビス(1-ナフチル)-1,3,4-オキサジアゾール、1,4-ビス[2-(5-フェニルオキサジアゾリル)]ベンゼン、1,4-ビス[2-(5-フェニルオキサジアゾリル)-4-tert-ブチルベンゼン]、2-(4'-tert-ブチルフェニル)-5-(4"-ビフェニル)-1,3,4-チアジアゾール、2,5-ビス(1-ナフチル)-1,3,4-チアジアゾール、1,4-ビス[2-(5-フェニルチアジアゾリル)]ベンゼン、2-(4'-tert-ブチルフェニル)-5-(4"-ビフェニル)-1,3,4-トリアゾール、2,5-ビス(1-ナフチル)-1,3,4-トリアゾール、1,4-ビス[2-(5-フェニルトリアゾリル)]ベンゼン等が挙げられるが、これらに限定されるものではない。

本発明の有機EL素子においては、有機層中に、一般式[1]～[18]の化合物の他に、発光材料、ドーピング材料、正孔注入材料および電子注入材料の少なくとも1種が同一層に含有されてもよい。また、本発明により得られた有機EL素子の、温度、湿度、雰囲気等に対する安定性の向上のために、素子の表面に保護層を設けたり、シリコンオイル、樹脂等により素子全体を保護することも可能である。

有機EL素子の陽極に使用される導電性材料としては、4eVより大きな仕事関数を持つものが適しており、炭素、アルミニウム、バナジウム、鉄、コバルト、ニッケル、タンクステン、銀、金、白金、パラジウム等およびそれらの合金、ITO基板、NEESA基板に使用される酸化スズ、酸化インジウム等の酸化金属、さらにはポリチオフェンやポリピロール等の有機導電性樹脂が用いられる。陰極に使用される導電性物質としては、4eVより小さな仕事関数を持つものが適

しており、マグネシウム、カルシウム、錫、鉛、チタニウム、イットリウム、リチウム、ルテニウム、マンガン、アルミニウム等およびそれらの合金が用いられるが、これらに限定されるものではない。合金としては、マグネシウム／銀、マグネシウム／インジウム、リチウム／アルミニウム等が代表例として挙げられるが、これらに限定されるものではない。合金の比率は、蒸着源の温度、雰囲気、真空中度等により制御され、適切な比率に選択される。陽極および陰極は、必要があれば二層以上の層構成により形成されていても良い。

本発明の有機EL素子においては、このようにして作製された一対の電極の少なくとも一方の表面に、カルコゲナイト層、ハロゲン化金属層又は金属酸化物層（以下、これらを表面層ということがある）を配置するのが好ましい。具体的には、発光媒体層側の陽極表面にケイ素やアルミニウムなどの金属のカルコゲナイト（酸化物を含む）層を、また、発光媒体層側の陰極表面にハロゲン化金属層又は金属酸化物層を配置するのがよい。これにより、駆動の安定化を図ることができる。

前記カルコゲナイトとしては、例えば $\text{SiO}_x$  ( $1 \leq X \leq 2$ )、 $\text{AlO}_x$  ( $1 \leq X \leq 1.5$ )、 $\text{SiON}$ 、 $\text{SiAlON}$ などが好ましく挙げられ、ハロゲン化金属としては、例えば $\text{LiF}$ 、 $\text{MgF}_2$ 、 $\text{CaF}_2$ 、フッ化希土類金属などが好ましく挙げられ、前記金属酸化物としては、例えば $\text{Cs}_2\text{O}$ 、 $\text{Li}_2\text{O}$ 、 $\text{MgO}$ 、 $\text{SrO}$ 、 $\text{BaO}$ 、 $\text{CaO}$ などが好ましく挙げられる。

さらに、本発明の有機EL素子においては、このようにして作製された一対の電極の少なくとも一方の表面に電子伝達化合物と還元性ドーパントの混合領域又は正孔伝達化合物と酸化性ドーパントの混合領域を配置するのも好ましい。このようにすることにより、電子伝達化合物が還元され、アニオンとなり混合領域が、より発光媒体に電子を注入、伝達しやすくなる。また、正孔伝達化合物は酸化され、カチオンとなり混合領域がより発光媒体に正孔を注入、伝達しやすくなる。好ましい酸化性ドーパントとしては、各種ルイス酸やアクセプター化合物が挙

げられる。好ましい還元性ドーパントとしては、アルカリ金属、アルカリ金属化合物、アルカリ土類金属、希土類金属及びこれらの化合物が挙げられる。

有機EL素子では、効率良く発光させるために、少なくとも一方の面は素子の発光波長領域において充分透明にすることが望ましい。また、基板も透明であることが望ましい。透明電極は、上記の導電性材料を使用して、蒸着やスパッタリング等の方法で所定の透光性が確保するように設定する。発光面の電極は、光透過率を10%以上にすることが望ましい。基板は、機械的、熱的強度を有し、透明性を有するものであれば限定されるものではないが、ガラス基板および透明性樹脂フィルムがある。透明性樹脂フィルムとしては、ポリエチレン、エチレン-酢酸ビニル共重合体、エチレン-ビニルアルコール共重合体、ポリプロピレン、ポリスチレン、ポリメチルメタアクリレート、ポリ塩化ビニル、ポリビニルアルコール、ポリビニルブチラール、ナイロン、ポリエーテルエーテルケトン、ポリサルホン、ポリエーテルサルファン、テトラフルオロエチレン-パーカルオロアルキルビニルエーテル共重合体、ポリビニルフルオライド、テトラフルオロエチレン-エチレン共重合体、テトラフルオロエチレン-ヘキサフルオロプロピレン共重合体、ポリクロロトリフルオロエチレン、ポリビニリデンフルオライド、ポリエステル、ポリカーボネート、ポリウレタン、ポリイミド、ポリエーテルイミド、ポリイミド、ポリプロピレン等が挙げられる。

本発明に係わる有機EL素子の各層の形成は、真空蒸着、スパッタリング、プラズマ、イオンプレーティング等の乾式成膜法やスピンドルコーティング、ディッピング、フローコーティング等の湿式成膜法のいずれの方法を適用することができる。膜厚は特に限定されるものではないが、適切な膜厚に設定する必要がある。膜厚が厚すぎると、一定の光出力を得るために大きな印加電圧が必要になり効率が悪くなる。膜厚が薄すぎるとピンホール等が発生して、電界を印加しても充分な発光輝度が得られない。通常の膜厚は5nmから10μmの範囲が適しているが、10nmから0.2μmの範囲がさらに好ましい。

湿式成膜法の場合、各層を形成する材料を、エタノール、クロロホルム、テトラヒドロフラン、ジオキサン等の適切な溶媒に溶解または分散させて薄膜を形成するが、その溶媒はいずれであっても良い。また、いずれの有機薄膜層においても、成膜性向上、膜のピンホール防止等のため適切な樹脂や添加剤を使用しても良い。使用の可能な樹脂としては、ポリスチレン、ポリカーボネート、ポリアリレート、ポリエステル、ポリアミド、ポリウレタン、ポリスルフォン、ポリメチルメタクリレート、ポリメチルアクリレート、セルロース等の絶縁性樹脂およびそれらの共重合体、ポリ-N-ビニルカルバゾール、ポリシラン等の光導電性樹脂、ポリチオフェン、ポリピロール等の導電性樹脂を挙げられる。また、添加剤としては、酸化防止剤、紫外線吸収剤、可塑剤等を挙げられる。

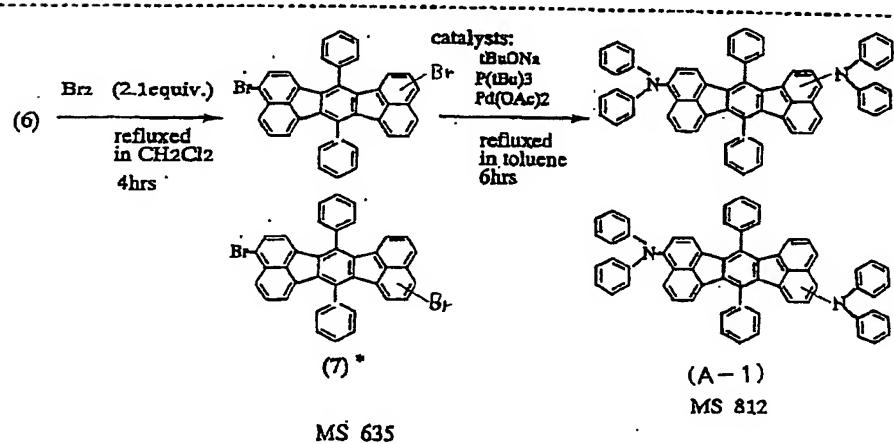
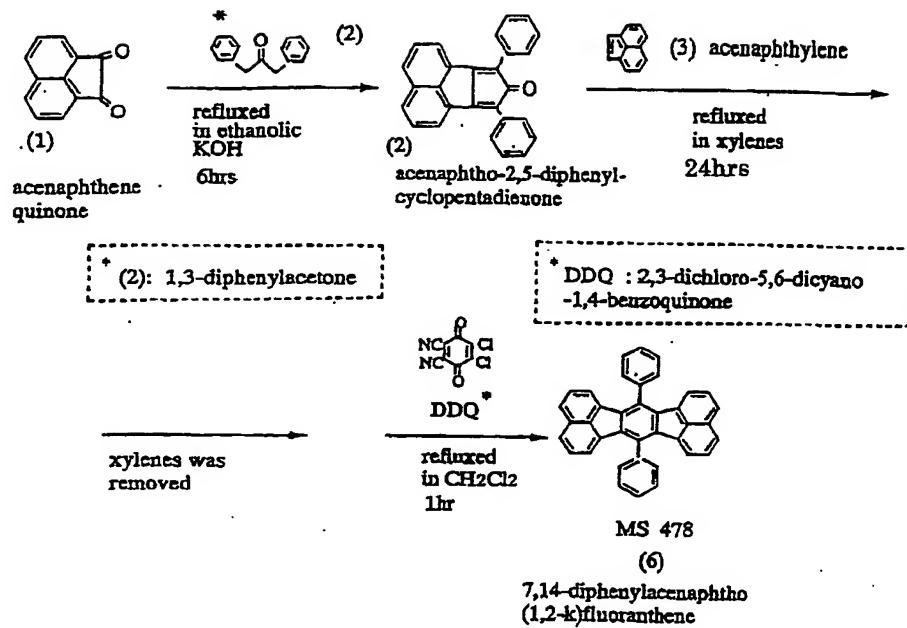
以上のように、有機EL素子の有機層に本発明の化合物を用いることにより、色純度及び発光効率が高く、寿命が長く、赤色系に発光する有機EL素子を得ることができる。

本発明の有機EL素子は、壁掛けテレビのフラットパネルディスプレイ等の平面発光体、複写機、プリンター、液晶ディスプレイのバックライト又は計器類等の光源、表示板、標識灯等に利用できる。

以下、本発明を合成例及び実施例に基づいてさらに詳細に説明する。

#### 合成例1（化合物A-1）

以下に示す反応経路によって、3,10-ビス(ジフェニルアミノ)-7,14-ジフェニルアセナフトフルオランテンを合成した。



\* (1) → (7)

cf. Jeff D. Debad, Allen J. Bard J. Am. Chem. Soc. vol.120 2476 (1998).

(A) 3, 10-及び 3, 11-ジプロモ-7, 14-ジフェニルアセナフター-  
[1, 2-k]フルオランテンの合成

J. B. Allen の方法により、アセトナフテンキノン (1) を出発原料とし、7, 14-ジフェニルアセナフター- [1, 2-k] フルオランテン (6) を

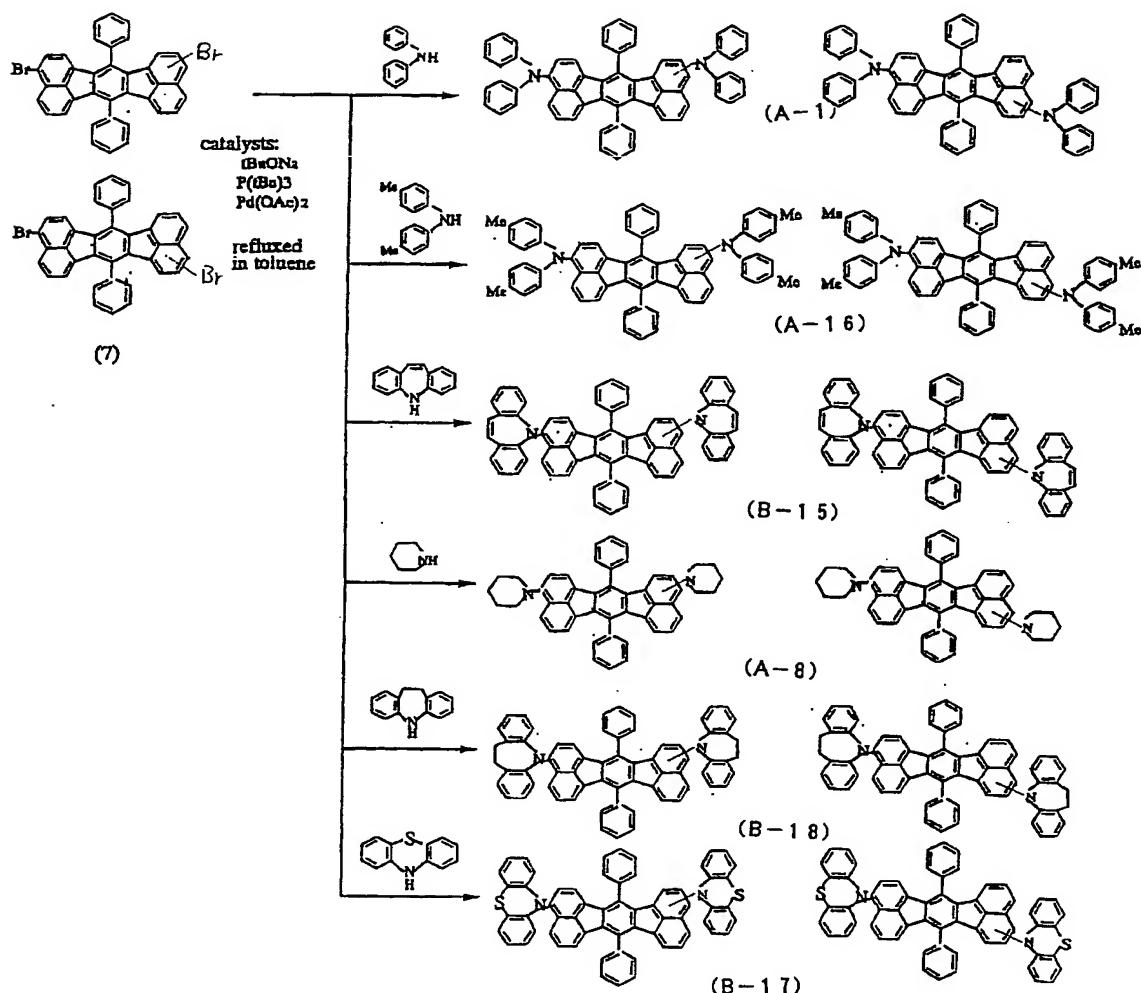
経て、3, 10-及び3, 11-ジプロモ-7, 14-ジフェニルアセナフト-[1, 2-k]フルオランテン(7)を合成した。3, 10-及び3, 11-ジプロモ-7, 14-ジフェニルアセナフト-[1, 2-k]フルオランテン(7)の化学構造は、FD-MS(フィールドディソーションマススペクトル)及び<sup>1</sup>H-NMRスペクトルにより同定した。<sup>1</sup>H-NMRスペクトルのケミカルシフトはAllenの測定値と一致した。(J. D. Debad, A. I. Bard J. Chem. Soc. vo 1. 120 2476(1998)参照)

(B) 3, 10-及び3, 11-ジフェニルアミノ-7, 14-ジフェニルアセナフトフルオランテン(化合物A-1)の合成

3, 10-及び3, 11-ジプロモ-7, 14-ジフェニルアセナフト-[1, 2-k]フルオランテン(7) 3. 5-6グラム(5. 6mmol)、ジフェニルアミン 1. 89グラム(11. 2mmol)、酢酸パラジウム 0. 06グラム(0. 3mmol)、トリーターシャリーブチルホスфин 0. 22グラム(1. 1mmol)、ソジウム-ターシャリーブトキサイド 1. 51グラム(14. 0mmol)をトルエン 150ミリリットルに室温で溶かし、6時間還流加熱して反応させた。反応液をろ過し、ろ液を濃縮して赤橙色の粉末状固体4. 8グラムを得た。トルエンに溶解した後、シリカゲルを充填したカラムクロマトグラムにより分別し、主成分4. 1グラムを得た。FD-MS(812)及び化合物(7)の構造より、3, 10-及び3, 11-ジフェニルアミノ-7, 14-ジフェニルアセナフトフルオランテン(化合物A-1)であることを確認した。また、反応液中の析出物もろ別したが、アセトン及び水で洗浄後、乾燥し0. 6グラムの粉末状固体を得た。FD-MS(812)及び<sup>1</sup>H-NMRスペクトルにより、ろ液からの分別物と同じ構造であると確認した。

同様に、3, 10-及び3, 11-ジアミノ-7, 14-ジフェニルアセナフト-[1, 2-k]フルオランテン類である、化合物A-16(合成例2)、化合物B-15(合成例3)、化合物A-8(合成例4)、化合物B-18(合成

例 5) 及び化合物 B-17 (合成例 6) の反応経路を以下に示す。



#### 合成例 2 (化合物 A-16)

合成例 1 (B)において、ジフェニルアミンの代わりに、*p*, *p*'-ジトリルアミン 2.31 グラム (11.7 mmol) を用いた以外は同様にして反応させた。反応後、反応溶液をろ過し、ろ液を水で洗浄した後、濃縮し、赤色の粉末状固体を得た。この固体を、シリカゲルを充填したカラムクロマトグラムにより分別し、高純度の主成分 2.9 グラムを得た。FD-M S (868) より、化合物 A-16 であると確認した。

### 合成例 3 (化合物B-15)

合成例1 (B)において、ジフェニルアミンの代わりに、イミノスチルベン2.27グラム(11.7mmol)を用いた以外は同様にして反応させた。反応後、反応溶液中に析出した生成物をろ過により分け、アセトン及び水による洗浄を繰り返した後、乾燥し、3.4グラムの赤橙色の粉末状固体を得た。この固体のテトラヒドロフラン溶液を、シリカゲルを充填した薄層クロマトグラフィーにより分取し、高純度の主成分2.3グラムを得た。FD-MS(862)より、化合物B-15であると確認した。

### 合成例 4 (化合物A-8)

合成例1 (B)において、ジフェニルアミンの代わりに、ピペリジン1.0グラム(11.7mmol)を用いた以外は同様にして反応させた。反応溶液をろ過し、ろ液を水で洗浄した後、濃縮し、赤色の粉末状固体を得た。この固体のトルエン溶液を、シリカゲルを充填したカラムクロマトグラフィーにより分取し、高純度の主成分2.1グラムを得た。FD-MS(644)より、化合物A-8であると確認した。

### 合成例 5 (化合物B-18)

合成例1 (B)において、ジフェニルアミンの代わりに、カルバゾール1.96グラム(11.7mmol)を用いた以外は同様にして反応させた。反応後、反応溶液中に析出した生成物をろ過により分け、アセトン及び水による洗浄を繰り返した後、乾燥し、3.8グラムの赤橙色の粉末状固体を得た。この固体のテトラヒドロフラン溶液を、シリカゲルを充填した薄層クロマトグラフィーにより分取し、高純度の主成分2.0グラムを得た。FD-MS(808)より、化合物B-18であると確認した。

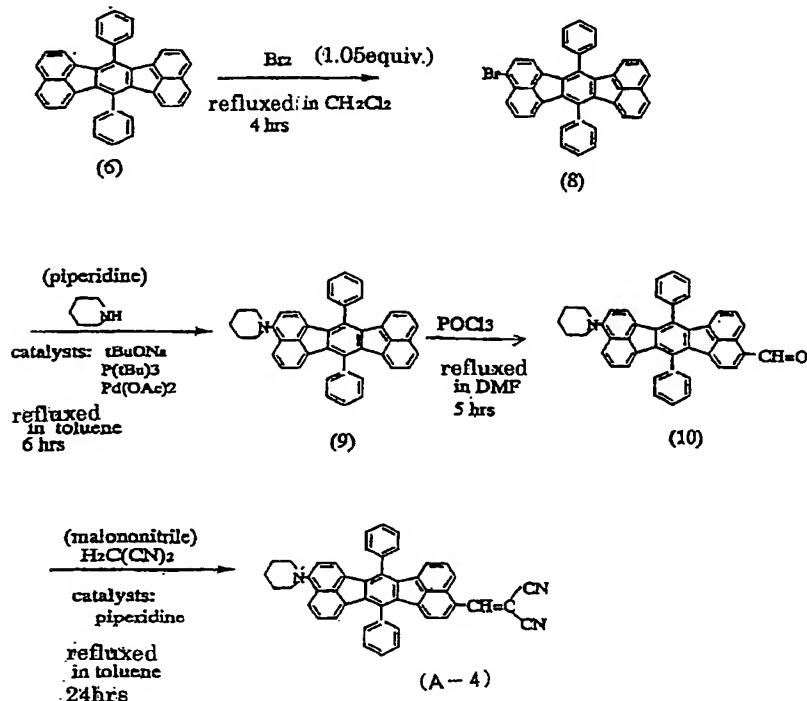
### 合成例 6 (化合物B-17)

合成例1 (B)において、ジフェニルアミンの代わりに、フェノチアジン2.33グラム(11.7mmol)を用いた以外は同様にして反応させた。反応

液を、ろ過し、ろ液を濃縮、乾燥し、4.2グラムの橙色の粉末状固体を得た。この固体のトルエン溶液を、シリカゲルを充填した薄層クロマトグラフィーにより分取し、高純度の主成分2.6グラムを得た。FD-MS(872)より、化合物B-17であると確認した。

#### 合成例7 (化合物A-4)

以下に示す反応経路によって、化合物A-4を合成した。



化合物(8)を合成する際の反応液の薄層クロマトグラフィーにより、化合物(6)のスポットが消失するまで反応させた。反応液を0.1N-NaOH水溶液で洗浄、濃縮後、シリカゲルを充填したカラムクロマトグラフィーにより分取して化合物(8)を得た。

合成例1(B)において、(7)の代わりに(8)を3.12グラム(5.6mmol)、ジフェニルアミンの代わりに、ピペリジン0.51グラム(11.5mmol)を用いた以外は同様にして反応させ、得られた固体のトルエン溶

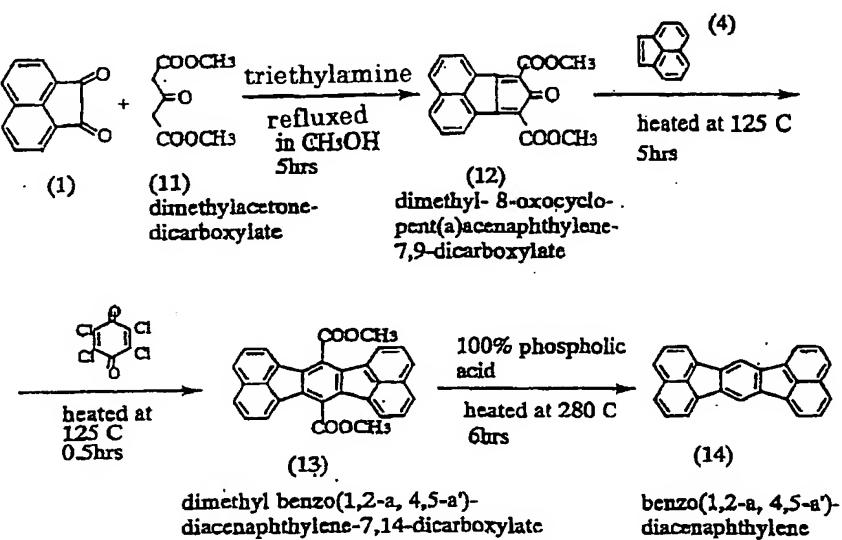
液を、シリカゲルを充填したカラムクロマトグラフィーにより分取し、高純度の化合物(9)を2.2グラム得た。

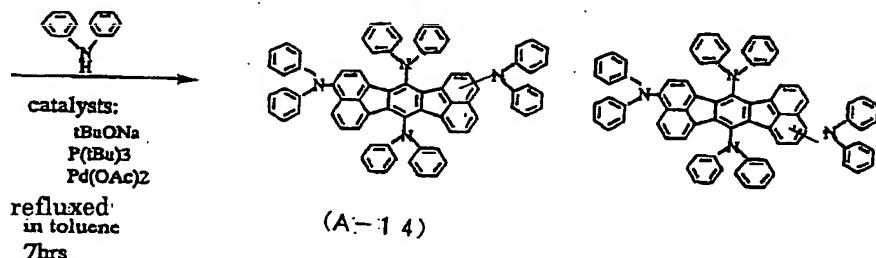
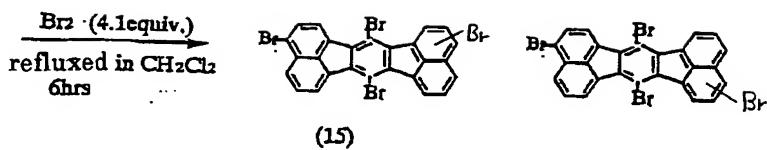
化合物(9) 5.61グラム(10.0mmol)を、ジメチルホルムアミド30ミリリットルに溶かし、オキシ塩化リン1.68グラム(11.0mmol)を加えて、加熱還流した。ろ液を、シリカゲルを充填したカラムクロマトグラフィーにより分別し、高純度の主成分4.0グラムを得た。F D - M S (589)より、化合物(10)であると確認した。

次に、化合物(10) 4.7グラム(8.0mmol)を、マロノニトニル0.7グラム(10.6mmol)と反応させた。反応溶液中に析出した生成物のテトラヒドロフラン溶液を、シリカゲルを充填した薄層クロマトグラフィーにより分取して、高純度で赤橙色の結晶3.6グラムを得た。F D - M S (637)より、化合物A-4であることを確認した。

#### 合成例8 (化合物A-14)

以下に示す反応経路によって、化合物A-14を合成した。(S. H. Tucker J. C hem. Soc. 1462(1958)参照)

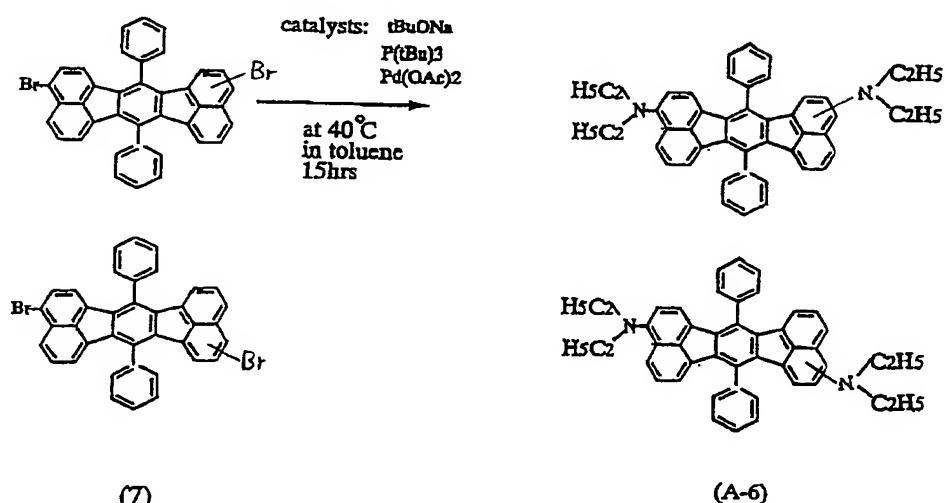




\* (1) → (14) cf. S. H. Tucker J. Chem. Soc.: 1462 (1958)

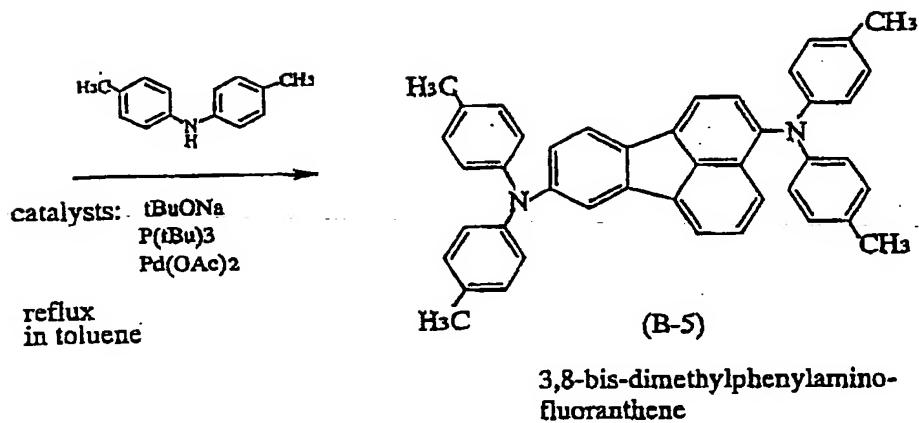
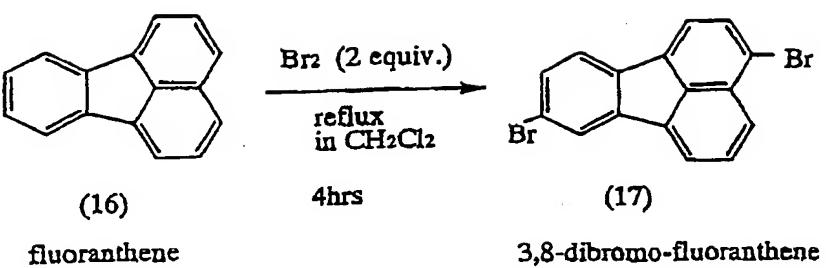
### 合成例 9 (化合物 A - 6 )

以下に示す反応経路によって、化合物 A-6 を合成した。



### 合成例 10 (化合物 B-5)

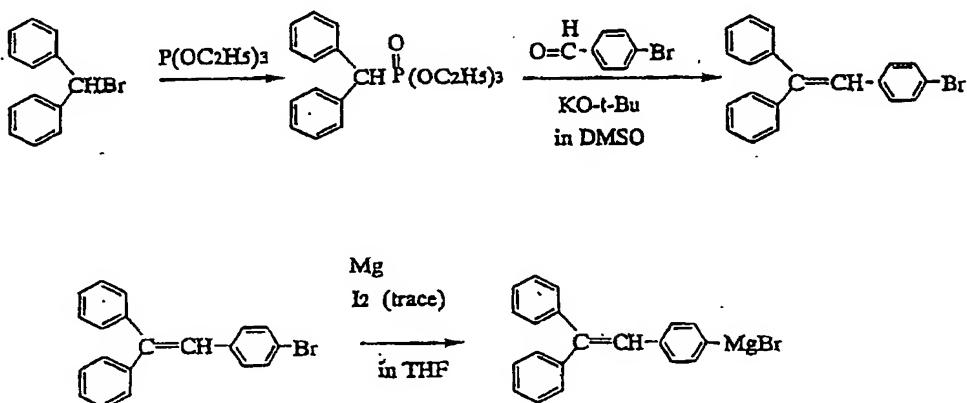
以下に示す反応経路によって、化合物 B-5 を合成した。(Beil. 5(3) 2278 参照)

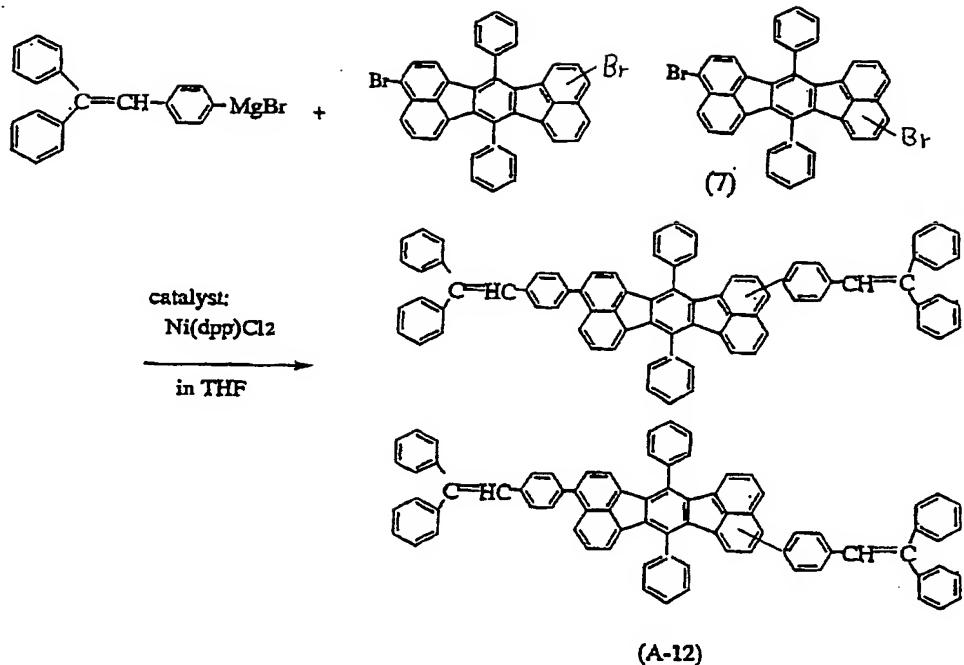


(16): cf. Beil. 5(3) 2278

### 合成例 1 1 (化合物 A - 1 2 )

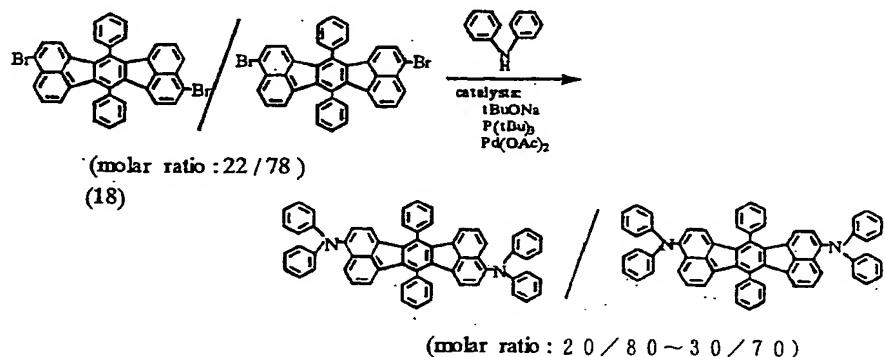
以下に示す反応経路によって、化合物 A - 1 2 を合成した。





### 合成例 1 2

以下に示す反応経路によって、3, 10-ビスジフェニルアミノ-7, 14-ジフェニルアセナフトー [1, 2-k] フルオランテン及び3, 11-ビスジフェニルアミノ-7, 14-ジフェニルアセナフトー [1, 2-k] フルオランテンのモル比が20/80～30/70の組成物を合成した。



(A) 3, 10-及び3, 11-ジブロモ-7, 14-ジフェニルアセナフトー

[1, 2-k] フルオランテン組成物 [組成物: 22/78] (18) の合成

合成例 1 (A) の反応液可溶部を濃縮し、テトロヒドロフランに全て溶解し再結晶した後、析出部分を除き、可溶部を濃縮してジブロモ化合物を得た。このジブロモ化合物は、3, 10-及び3, 11-ジブロモ-7, 14-ジフェニルアセナフトー [1, 2-k] フルオランテンのモル比が 22/78 であることを <sup>1</sup>H-NMRスペクトルにより確認した。

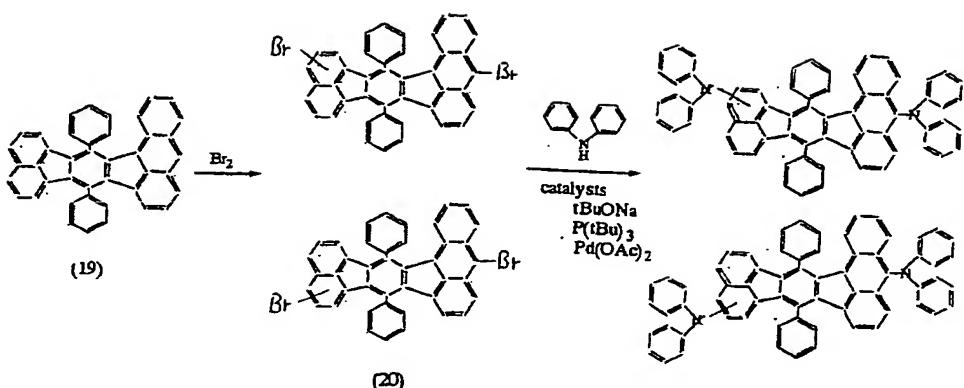
(B) 3, 10-及び3, 11-ジフェニルアミノ-7, 14-ジフェニルアセナフトー [1, 2-k] フルオランテン組成物 [モル比: 20~30/80~70] の合成

3, 10-及び3, 11-ジブロモ-7, 14-ジフェニルアセナフトー [1, 2-k] フルオランテン組成物 [モル比: 22/78] (18) 5.00グラム (7.9mmol)、ジフェニルアミン 2.78グラム (16.5mmol)、酢酸パラジウム 0.09グラム (0.09mmol)、トリーターシャリーブチルホスфин 0.44グラム (2.2mmol)、ソジウムターシャリーブトキサイド 2.12グラム (19.6mmol) をトルエン 100ミリリットルに溶かし、6時間還流加熱して反応させた。反応液をろ過し、ろ液の濃縮液をシリカゲルを充填したカラムクロマトグラムにより分別し、赤橙色の粉末状固体 6.20グラムを得た。FD-MS (812) 及び <sup>1</sup>H-NMRスペクトル (H: 400MHz、測定溶媒: DMSO (120°C)、図1参照) により、3, 10-ビス-ジフェニルアミノ-7, 14-ジフェニルアセナフトー [1, 2-k] フルオランテンと 3, 11-ビス-ジフェニルアミノ-7, 14-ジフェニルアセナフトー [1, 2-k] フルオランテン (A-1) のモル比が 20/80~30/70 の組成物であると確認した。

### 合成例 1 3

以下に示す反応経路によって、5, 12-及び/又は5, 13-ビス-ジフェニルアミノ-9, 16-ジフェニルフルオランテノ [8, 9-a] アセアント

リレンを合成した。



(A) 9, 16-ジフェニルフルオランテノ [8, 9-a] アセアントリレン (19) の合成

9, 16-ジフェニルフルオランテノ [8, 9-a] アセアントリレンは、  
Bandyopadhyai の方法を参考にして、アセアントリレンキノンを出  
発原料とした 1, 3-ジフェニルシクロペンタ [a] アセアントリレン-2-オ  
ンとアセナフチレンとの反応により合成した。[Indian J. Chem. Vol. 21B, 91 (1982)  
) 参照]

(B) 5, 12-及び／又は 5, 13-ジブロモ-9, 16-ジフェニルフル  
オランテノ [8, 9-a] アセアントリレン (20) の合成

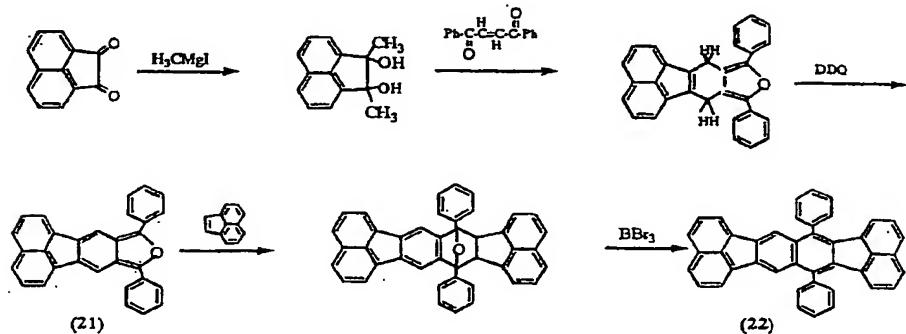
9, 16-ジフェニルフルオランテノ [8, 9-a] アセアントリレン (1  
9) 4.00 グラム (7.6 mmol) を塩化メチレン 240 ミリリットルに  
溶かし、還流加熱しながら臭素の 1M 塩化メチレン溶液 18.0 ミリリットル  
を滴下し、2 時間反応させた。反応液はカ性ソーダ水溶液と純水で洗浄し、濃縮  
して 5.06 グラムの黄褐色粉末状固体を得た。この化合物は、FD-MS (6  
86) 及び <sup>1</sup>H-NMR スペクトルにより、5, 12-ジブロモ-9, 16-ジ  
フェニルフルオランテノ [8, 9-a] アセアントリレン及び／又は 5, 13  
-ジブロモ-9, 16-ジフェニルフルオランテノ [8, 9-a] アセアント  
リレンと確認した。

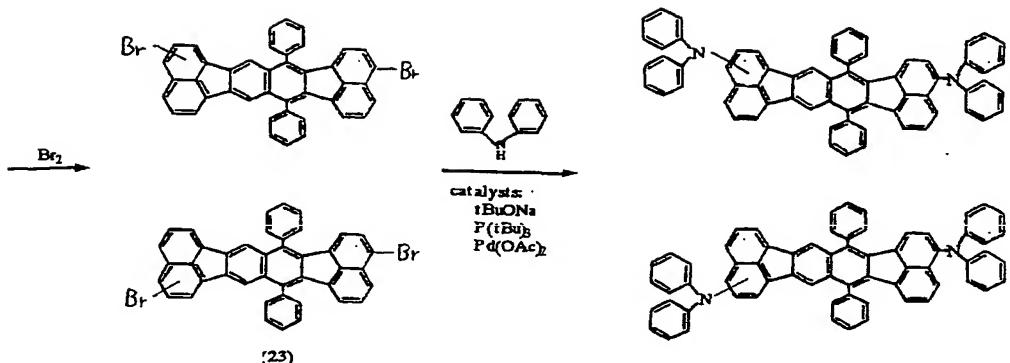
(C) 5, 12-及び/又は5, 13-ビスージフェニルアミノ-9, 16-ジフェニルフルオランテノ[8, 9-a]アセアントリレンの合成

5, 12-及び/又は5, 13-ジプロモ-9, 16-ジフェニルフルオランテノ[8, 9-a]アセアントリレン(20) 5. 00グラム(7. 4mmol)、ジフェニルアミン 2. 75グラム(16. 2mmol)、酢酸パラジウム 0. 09グラム(0. 4mmol)、トリーターシャリーブチルホスフィン 0. 43グラム(2. 2mmol)、ソジウムターシャリーブトキサイド 2. 05グラム(20. 6mmol)をトルエン 200ミリリットルに溶かし、5時間還流加熱して反応させた。反応液をろ過し、ろ液の濃縮液をシリカゲルを充填したカラムクロマトグラムにより精製し、黒紫色の粉末状の主成分 4. 27グラムを得た。この化合物は、FD-MS(862)及び<sup>1</sup>H-NMRスペクトル(H: 400MHz、測定溶媒: DMSO(120℃)、図2参照)により、5, 12-及び/又は5, 13-ビスージフェニルアミノ-9, 16-ジフェニルフルオランテノ[8, 9-a]アセアントリレンであると確認した。

#### 合成例14

以下に示す反応経路によって、3, 11-及び/又は3, 12-ビスージフェニルアミノ-7, 16-ジフェニルフルオランテノ[8, 9-k]フルオランテンを合成した。





(A) 2, 5-ジフェニルフルオランテノ [11', 12' - 3, 4] フラン (21) の合成

S. H. T u c k e r の方法 [J. Chem. Soc., 1462 (1958)] を参考にして合成した 7, 8-ジメチルアセナフテン-7, 8-ジオールとトランス-1, 2-ジベンゾイルエチレンを N. C a m p b e l l の方法 [J. Chem. Soc., 1555 (1949)] で反応させて 2, 5-ジフェニルフルオランテノ [11', 12' - 3, 4] フラン (21) を合成した。

(B) 7, 16-ジフェニルフルオランテノ [8, 9-k] フルオランテン (22) の合成

2, 5-ジフェニルフルオランテノ [11', 12' - 3, 4] フラン (21) 5.00 グラム (12.7 mmol) とアセナフチレン 3.86 グラム (19.0 mmol) をキシレン 500 ミリリットルと塩化メチレン 660 ミリリットルの混合溶媒に加え 3 時間、還流加熱した。この溶液を冷却して  $\text{Br}_3$  の 1 M 塩化メチレン溶液 16.0 ミリリットルを滴下し、さらに 4 時間 60°C で加熱した。反応液は炭酸水素ナトリウム水溶液および純水で洗浄し、濃縮液をシリカゲルを充填したカラムクロマトグラムにより精製し、3.20 グラムの黄色結晶を得た。この化合物は、F D - M S (528) 及び  $^1\text{H-NMR}$  スペクトルにより、7, 16-ジフェニルフルオランテノ [8, 9-k] フルオラ

ンテン（22）であると確認した。

(C) 3, 11-及び／又は3, 12-ジプロモ-7, 16-ジフェニルフルオランテノ〔8, 9-k〕フルオランテン（23）の合成

7, 16-ジフェニルフルオランテノ〔8, 9-k〕フルオランテン（22）2.30グラム（4.3mmol）を塩化メチレン230ミリリットルに溶かし、還流加熱しながら臭素の1M塩化メチレン溶液9.0ミリリットルを滴下し、さらに2時間反応させた。反応液はカ性ソーダ水溶液および純水で洗浄、濃縮して3.06グラムの淡黄褐色結晶を得た。この化合物は、FD-M S（686）及び<sup>1</sup>H-NMRスペクトルにより、3, 11-及び／又は3, 12-ジプロモ-7, 16-ジフェニルフルオランテノ〔8, 9-k〕フルオランテン（23）であると確認した。

(D) 3, 11-及び／又は3, 12-ビス-ジフェニルアミノ-7, 16-ジフェニルフルオランテノ〔8, 9-k〕フルオランテンの合成

3, 11-及び／又は3, 12-ジプロモ-7, 16-ジフェニルフルオランテノ〔8, 9-k〕フルオランテン（23）3.92グラム（5.7mmol）、ジフェニルアミン2.03グラム（12.0mmol）、酢酸パラジウム0.07グラム（0.07mmol）、トリーターシャリーブチルホスフィン0.33グラム（1.7mmol）、ソジウムターシャリーブトキサイド1.56グラム（14.4mmol）をトルエン120ミリリットルに溶かし、6時間還流加熱して反応させた。反応液をろ過し、ろ液をシリカゲルを充填したカラムクロマトグラムにより精製し、橙色粉末状結晶4.27グラムを得た。この化合物は、FD-M S（862）及び<sup>1</sup>H-NMRスペクトル（H: 400 MHz、測定溶媒：DMSO（120℃）、図3参照）により、3, 11-及び／又は3, 12-ビス-ジフェニルアミノ-7, 16-ジフェニルフルオランテノ〔8, 9-k〕フルオランテンであると確認した。

#### 合成例15

3, 10-ビス(ジトリルアミノ)-7, 14-ジフェニルアミノアセナフト-  
 [1, 2-k]フルオランテン及び3, 11-ビス(ジトリルアミノ)-7, 14-  
 デジフェニルアミノアセナフト- [1, 2-k]フルオランテンのモル比が80  
 /20~90/10の組成物を合成した。

(A) 3, 10-及び3, 11-ジブロモ-7, 14-ジフェニルアセナフト-  
 [1, 2-k]フルオランテン組成物 (18) の合成

合成例1 (A) の反応液可溶部を濃縮し、テトロヒドロフランに全て溶解し再結晶した後、析出部分を除き、可溶部を濃縮してジブロモ化合物を得た。このジブロモ化合物は、3, 10-及び3, 11-ジブロモ-7, 14-ジフェニルアセナフト- [1, 2-k]フルオランテンのモル比が80:20~90:10であることを<sup>1</sup>H-NMRスペクトルにより確認した。

(B) 3, 10-及び3, 11-ビス(ジトリルアミノ)-7, 14-ジフェニルアセナフト- [1, 2-k]フルオランテンのモル比が80/20~90/10の組成物の合成

合成例12 (B)において、ジフェニルアミンの代わりにジ-p, p-ジトリルアミンを用いたことを除き同様にして、異性体のモル比80/20~90/10の3, 10-及び3, 11-ビス(ジトリルアミノ)-7, 14-ジフェニルアセナフト- [1, 2-k]フルオランテン (A-16) を合成した。

#### 合成例16

3, 10-ビス(ジフェニルアミノ)-7, 14-ジフェニルアミノアセナフト- [1, 2-k]フルオランテン及び3, 11-ビス(ジフェニルアミノ)-7, 14-ジフェニルアミノアセナフト- [1, 2-k]フルオランテンのモル比が80/20~90/10の組成物を合成した。

(A) 3, 10-及び3, 11-ジブロモ-7, 14-ジフェニルアセナフト- [1, 2-k]フルオランテン組成物 (18) の合成

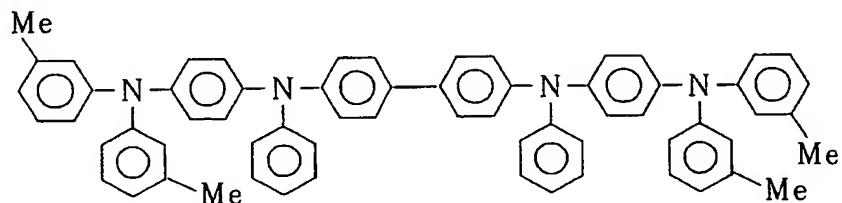
合成例15 (A)と同様にしてジブロモ化合物を得た。

(B) 3, 10-及び 3, 11-ビス(ジフェニルアミノ)-7, 14-ジフェニルアセナフート-[1, 2-k]フルオランテン (A-1) のモル比が 80/20 ~ 90/10 の組成物の合成

(A) で得られたジプロモ化合物を用い、合成例 12 (B) と同様にして、3, 10-ジフェニルアミノ-7, 14-ジフェニルアセナフート-[1, 2-k]フルオランテンと 3, 11-ジフェニルアミノ-7, 14-ジフェニルアセナフート-[1, 2-k]フルオランテンのモル比が 80/20 ~ 90/10 の組成物を合成した。

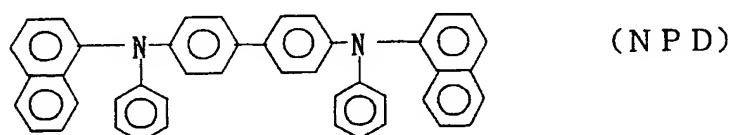
### 実施例 1

洗浄した ITO 電極付きガラス板上に、正孔注入材として下記化合物 (H 232) を膜厚 60 nm で蒸着した。



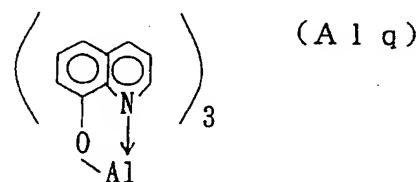
(H 232)

次に、正孔輸送材として下記化合物 (NPD) を膜厚 20 nm で蒸着した。



(NPD)

次に、発光層として 8-ヒドロキシキノリンの Al 錯体 (Alq)



(Alq)

と3, 10-及び3, 11-ジフェニルアミノ-7, 14-ジフェニルアセナフトフルオランテン（化合物A-1）を、化合物A-1の濃度が2. 1 mol%となるように膜厚50 nmで蒸着した。さらに電子注入層としてAl<sub>x</sub>のみを膜厚10 nmで蒸着し、その上に無機化合物層としてLiFを膜厚0. 2 nmで蒸着後、アルミニウムを膜厚170 nm蒸着し電極を形成して有機EL素子を得た。各層は10<sup>-6</sup> Torrの真空中で、基板温度室温の条件下で蒸着した。

この素子の発光特性は、直流電圧5. 5 Vの印加電圧で発光輝度103 (cd/m<sup>2</sup>)、発光効率は6. 2 (cd/A)と高効率であった。色度座標が(0. 56, 0. 44)と橙色発光であった。また、初期発光輝度500 (cd/m<sup>2</sup>)で、定電流駆動したところ半減寿命は2600時間と長寿命であった。

本実施例は、化合物A-1をドーピング材料として用いると、高性能の有機EL素子を実現できることを示している。発光スペクトルを測定したところドーピング材料の蛍光スペクトルと一致し、ドーピング材料が発光中心として働いていたことが判明した。

#### 比較例1

実施例1において、化合物A-1の代わりにルブレンを濃度が4. 0 mol%となるように蒸着した以外は同様にして、有機EL素子を得た。

この素子の発光特性は、直流電圧5. 5 Vの印加電圧で発光輝度105 (cd/m<sup>2</sup>)、発光効率は7. 6 (cd/A)であったが、色度座標(0. 50, 0. 50)の黄色発光であった。初期発光輝度500 (cd/m<sup>2</sup>)で、定電流駆動したところ半減寿命は1000時間と実施例1よりも短かった。

#### 比較例2

実施例1において、化合物A-1の代わりに、特開平11-40360号公報記載のフルオランテノ[8, 9-k]フルオランテンを濃度が2 mol%となるように蒸着した以外は同様にして、有機EL素子を得た。

この素子の発光特性は、直流電圧5. 5 Vの印加電圧で発光輝度35 (cd/

$\text{m}^2$ )、発光効率は 3.0 ( $\text{cd}/\text{A}$ ) であり、黄緑色発光であった。初期発光輝度 500 ( $\text{cd}/\text{m}^2$ ) で、定電流駆動したところ半減寿命は 300 時間と短かった。

### 比較例 3

実施例 1において、化合物 A-1 の代わりに、特開平 11-168445 号公報記載の 7,14-ジフェニルアセナフト [1,2-k] フルオランテンを濃度が 2 mol% となるように蒸着した以外は同様にして、有機 EL 素子を得た。

この素子の発光特性は、直流電圧 6 V の印加電圧で発光輝度 69 ( $\text{cd}/\text{m}^2$ )、発光効率は 1.3 ( $\text{cd}/\text{A}$ ) であり、黄緑色発光であったが、Alq 単独を発光させるより効率が減少した。初期発光輝度 500 ( $\text{cd}/\text{m}^2$ ) で、定電流駆動したところ半減寿命は 400 時間と短かった。また、素子の発光スペクトルを計測したところ、素子の発光スペクトルはドーピング材料の蛍光スペクトルと一致しておらず、上記化合物は発光しておらず黄緑色発光も Alq からのものであることが判明し、ドーピング材料は発光材料として機能していなかった。

### 実施例 2～11

実施例 1において、化合物 A-1 の代わりに、表 1 に示す化合物を蒸着した以外は同様にして、有機 EL 素子を得た。

この素子の発光特性を実施例 1 と同様にして測定し、測定時の印加電圧、発光輝度、発光効率、発光色及び初期発光輝度 500 ( $\text{cd}/\text{m}^2$ ) で、定電流駆動した半減寿命を表 1 に示す。

### 実施例 12

実施例 1において、発光層に合成例 1.2 で得られた異性体比が一定の化合物 (A-1) の濃度を 100% とし、Alq を含有させなかつこと以外は同様にして、有機 EL 素子を得た。

この素子の発光特性は、直流電圧 4.5 V の印加電圧で発光輝度 80 ( $\text{cd}/\text{m}^2$ )、発光効率は 3.5 ( $\text{cd}/\text{A}$ ) であった。初期発光輝度 500 ( $\text{cd}/\text{m}^2$ )

?)で、定電流駆動したところ半減寿命は2100時間と長かった。このように、実施例1と比較しても長寿命であり、主たる発光材料としても使用できる。

### 実施例1 3

実施例1において、化合物(A-1)の代わりに、合成例15で得られた異性体比が一定の化合物(A-16)を用いたこと以外は同様にして、有機EL素子を得た。

この素子の発光特性は、直流電圧5.5Vの印加電圧で発光輝度94(cd/m<sup>2</sup>)、発光効率は5.94(cd/A)、色度座標(0.60, 0.39)の赤橙色発光であった。初期発光輝度500(cd/m<sup>2</sup>)で、定電流駆動したところ半減寿命は3200時間と長かった。

### 実施例1 4

実施例1において、化合物(A-1)の代わりに、合成例16で得られた異性体比が一定の化合物(A-1)を用いたこと以外は同様にして、有機EL素子を得た。

この素子の発光特性は、直流電圧6Vの印加電圧で発光輝度100(cd/m<sup>2</sup>)、発光効率は4.75(cd/A)、色度座標(0.58, 0.42)であった。初期発光輝度500(cd/m<sup>2</sup>)で、定電流駆動したところ半減寿命は1800時間と長かった。この化合物を用いることにより、実施例1に比較して赤味を増すことができた。これは、異性体のうち長波長発光が可能となる3,11-ビスージフェニルアミノ-7,14-ジフェニルアセナフト-[1,2-k]フルオランテンが多く含まれているためである。

表 1

		化合物	電 壓 (V)	発光輝度 (cd/m <sup>2</sup> )	発光効率 (cd/A)	発光色	半減寿命 (時間)
実 施 例	2	A-2	5. 5	140	5. 7	赤橙色	2800
	3	A-8	5. 8	120	3. 6	橙色	2100
	4	A-14	5. 2	120	6. 1	赤色	2700
	5	A-16	6. 0	170	4. 7	赤橙色	3100
	6	B-3	6. 0	160	3. 2	赤橙色	1900
	7	B-15	5. 5	130	2. 8	橙色	1800
	8	B-17	5. 8	110	2. 0	赤橙色	1700
	9	B-18	6. 1	120	2. 8	赤橙色	2000
	10	A-4	7. 2	110	3. 7	赤色	1000
	11	B-5	6. 0	120	6. 7	黄緑色	1800

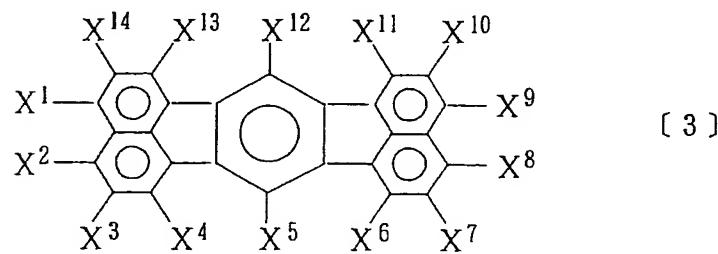
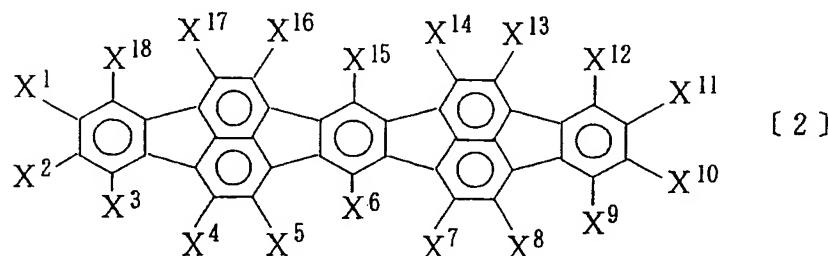
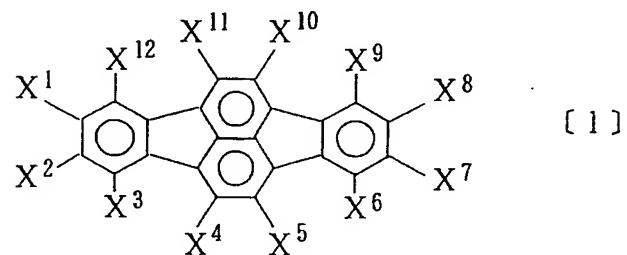
産業上の利用可能性

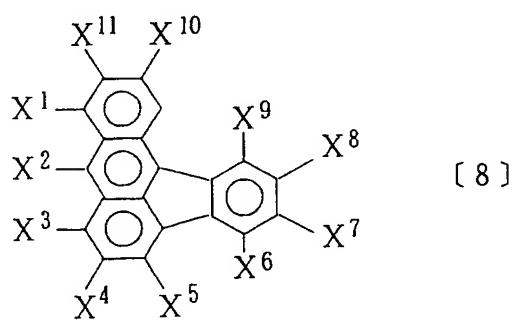
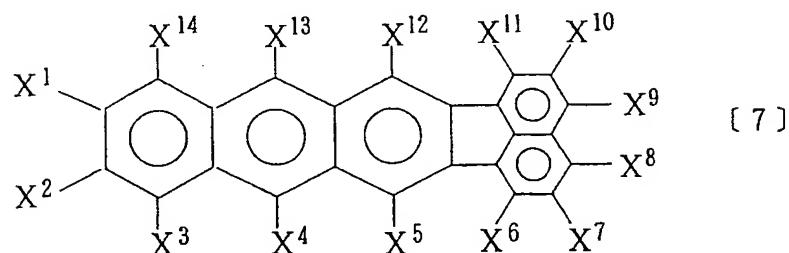
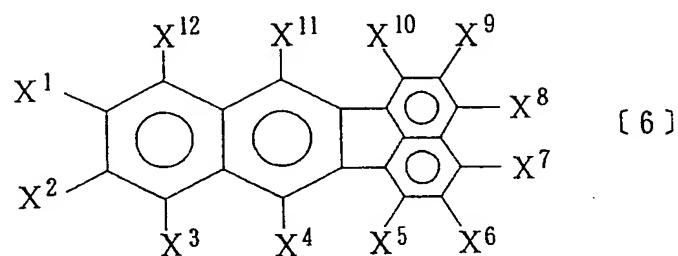
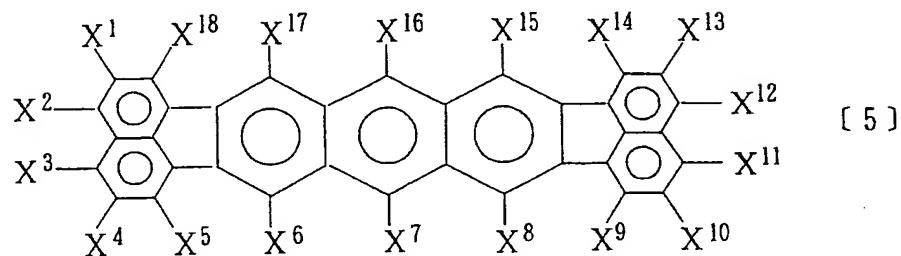
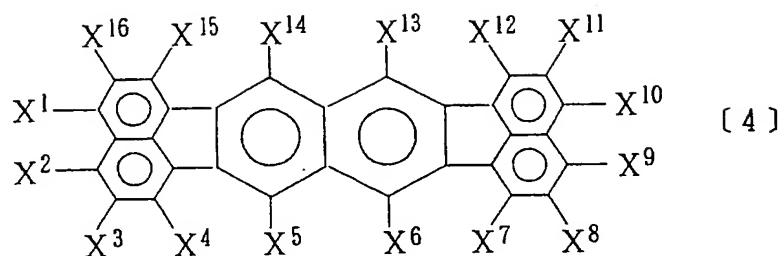
以上、詳細に説明したように、上記〔1〕～〔18〕で示される化合物を利用した本発明の有機エレクトロルミネッセンス素子は、黄色～赤色系に発光し、色純度及び発光効率が高く、寿命も長い。

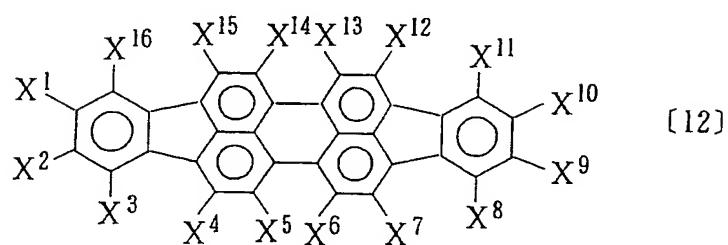
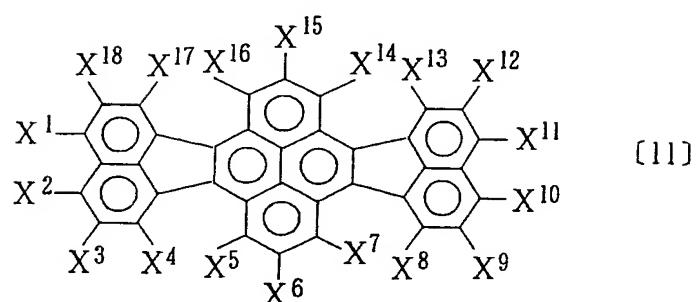
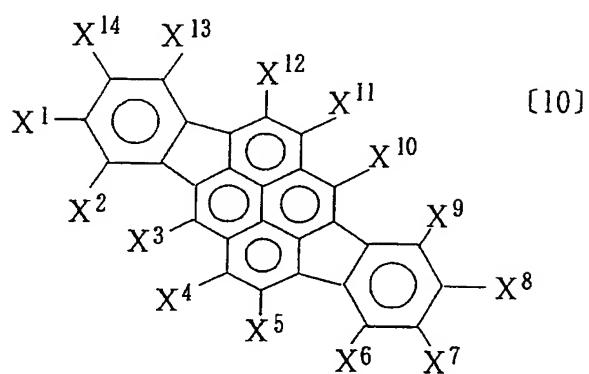
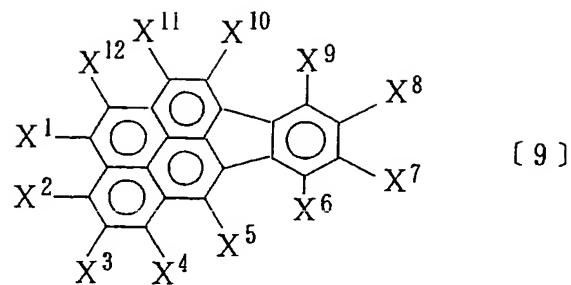
このため、本発明の有機エレクトロルミネッセンス素子は、壁掛テレビの平面発光体やディスプレイのバックライト等の光源として有用である。

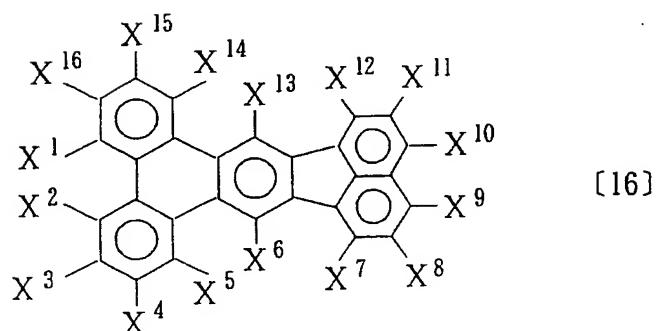
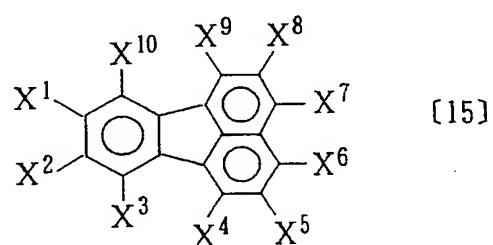
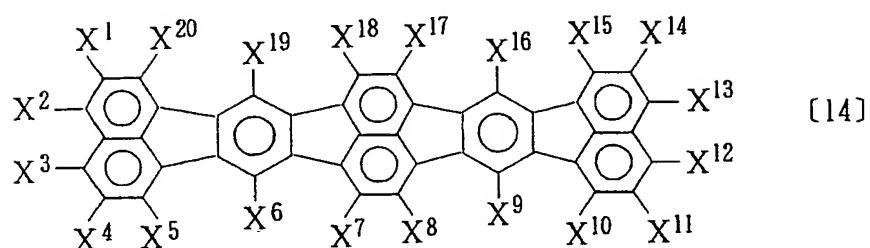
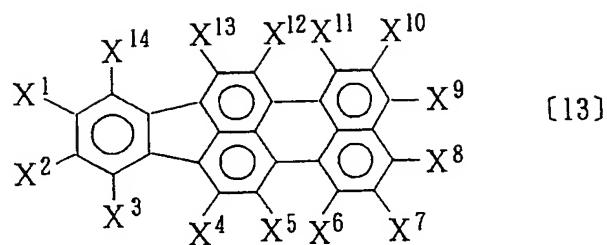
## 請求の範囲

1. 少なくとも一対の電極間に有機層が設けられた有機エレクトロルミネッセンス素子であって、該有機層に、含フルオランテン骨格に少なくともアミン又はアルケニル基が置換されている化合物を含有することを特徴とする有機エレクトロルミネッセンス素子。
2. 前記化合物が、下記一般式〔1〕～〔18〕のいずれかで示される化合物であることを特徴とする請求項1に記載の有機エレクトロルミネッセンス素子。



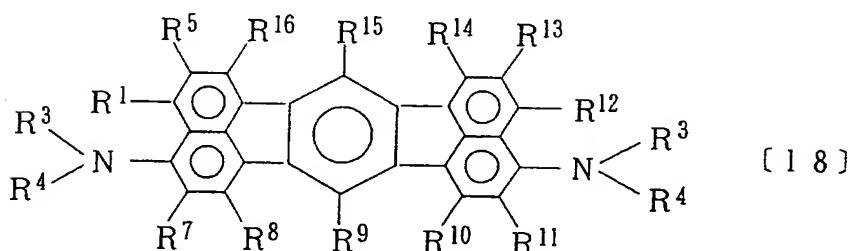
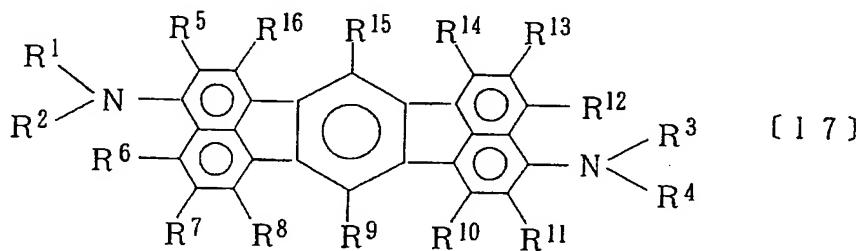






[一般式 [1] ~ [16] 式中、X<sup>1</sup> ~ X<sup>20</sup>は、それぞれ独立に、水素原子、直鎖、分岐もしくは環状の炭素原子数 1 ~ 20 のアルキル基、直鎖、分岐もしくは

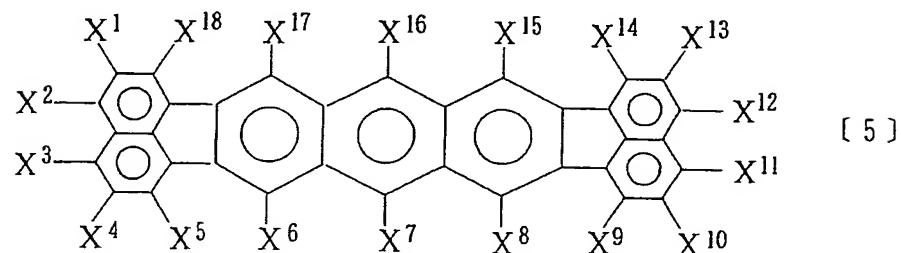
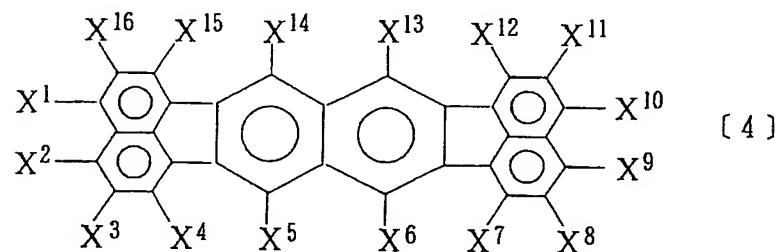
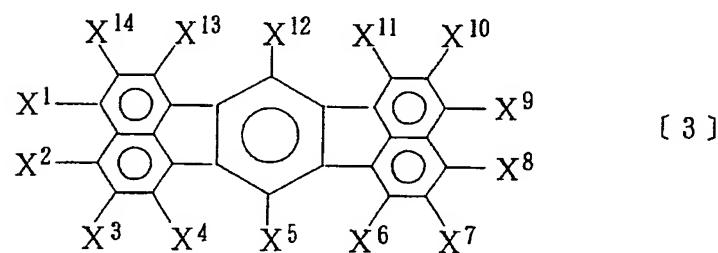
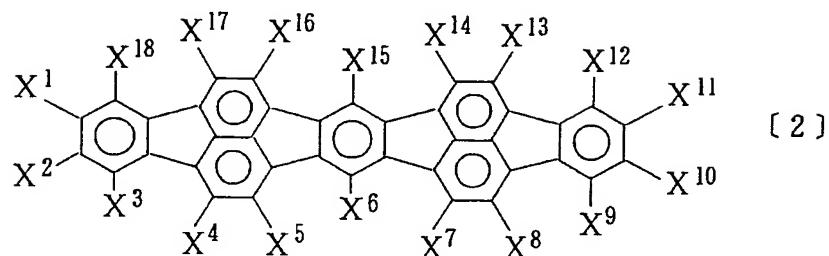
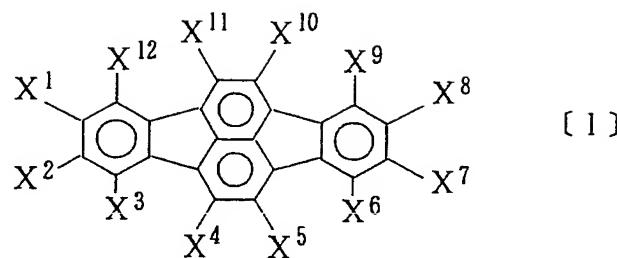
環状の炭素原子数1～20のアルコキシ基、置換もしくは無置換の炭素原子数6～30のアリール基、置換もしくは無置換の炭素原子数6～30のアリールオキシ基、置換もしくは無置換の炭素原子数6～30のアリールアミノ基、置換もしくは無置換の炭素原子数1～30のアルキルアミノ基、置換もしくは無置換の炭素原子数7～30のアリールアルキルアミノ基又は置換もしくは無置換炭素原子数8～30のアルケニル基であり、隣接する置換基及び $X^1 \sim X^{20}$ は結合して環状構造を形成していてもよい。隣接する置換基がアリール基の時は、置換基は同一であってもよい。ただし、各式中の置換基 $X^1 \sim X^i$  ( $i = 12 \sim 20$ ) の少なくとも一つはアミン又はアルケニル基を含有する。】

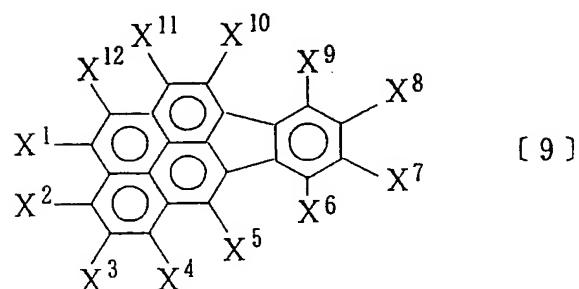
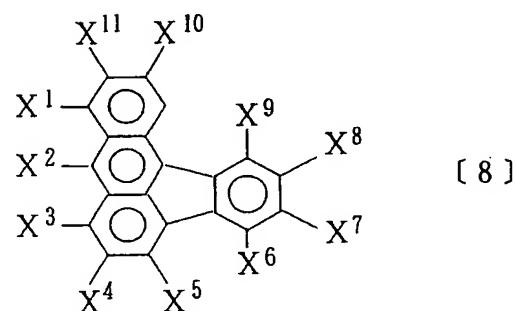
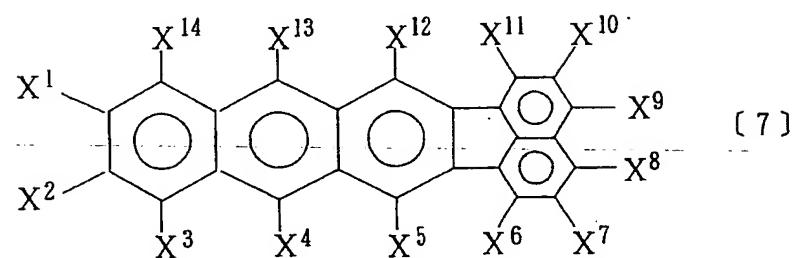
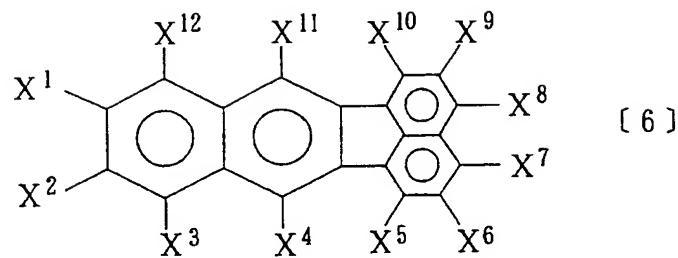


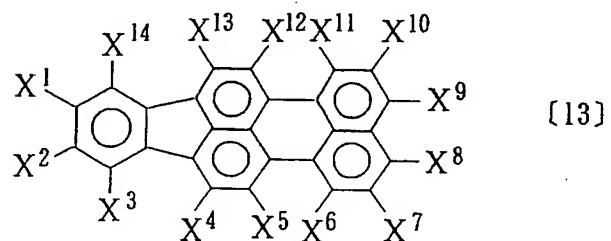
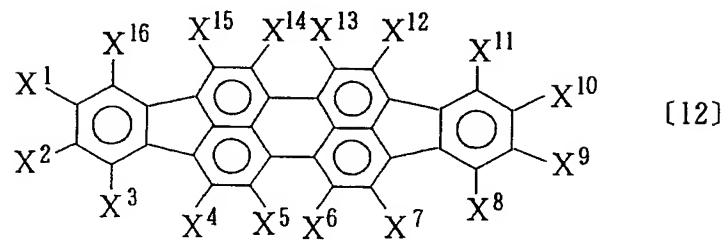
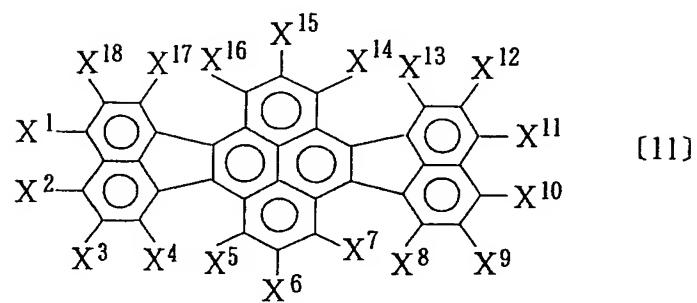
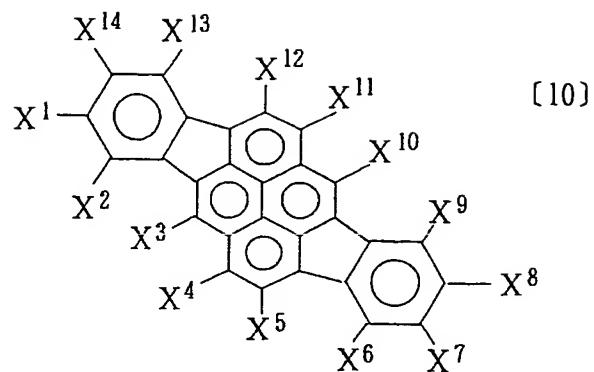
〔一般式〔17〕～〔18〕式中、 $R^1 \sim R^4$  は、それぞれ独立に、炭素原子数1～20のアルキル基、置換もしくは無置換の炭素原子数6～30のアリール基であり、 $R^1$ と $R^2$ 及び／又は $R^3$ と $R^4$ は、炭素-炭素結合又は $-O-$ 、 $-S-$ を介して結合していてもよい。 $R^5 \sim R^{16}$ は、水素原子、直鎖、分岐もしくは環状の炭素原子数1～20のアルキル基、直鎖、分岐もしくは環状の炭素原子数

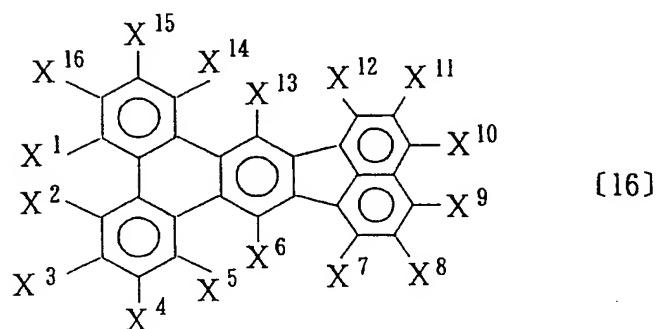
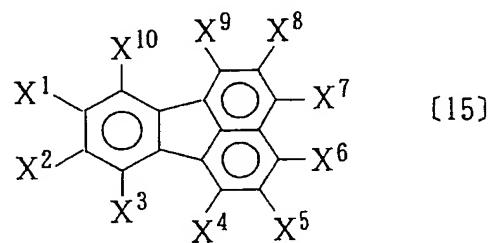
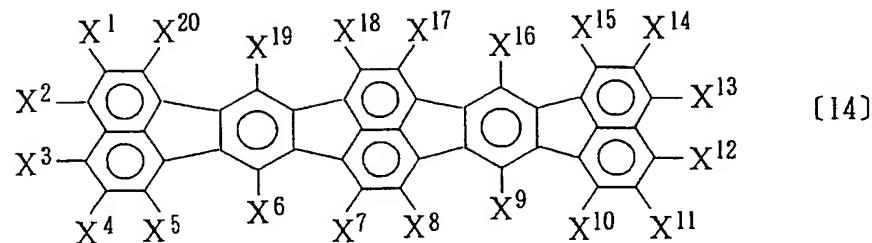
1～20のアルコキシ基、置換もしくは無置換の炭素原子数6～30のアリール基、置換もしくは無置換の炭素原子数6～30のアリールオキシ基、置換もしくは無置換の炭素原子数6～30のアリールアミノ基、置換もしくは無置換の炭素原子数1～30のアルキルアミノ基、置換もしくは無置換の炭素原子数7～30のアリールアルキルアミノ基又は置換もしくは無置換炭素原子数8～30のアルケニル基であり、隣接する置換基及びR<sup>5</sup>～R<sup>16</sup>は結合して環状構造を形成してもよい。ただし、各式中の置換基R<sup>5</sup>～R<sup>16</sup>の少なくとも一つはアミン又はアルケニル基を含有する。】

3. 前記有機層が、正孔輸送層及び／又は発光層であることを特徴とする請求項1又は2に記載の有機エレクトロルミネッセンス素子。
4. 前記有機層に、一般式〔1〕～〔18〕で示される化合物が、濃度1～70重量%で含有されていることを特徴とする請求項1に記載の有機エレクトロルミネッセンス素子。
5. 前記有機層と電極との間に無機化合物層を設けたことを特徴とする請求項1～4のいずれかに記載の有機エレクトロルミネッセンス素子。
6. 赤色系の発光をすることを特徴とする請求項1～5のいずれかに記載の有機エレクトロルミネッセンス素子。
7. 前記有機層に、前記化合物と前記化合物の異性体とを含有することを特徴とする請求項1に記載の有機エレクトロルミネッセンス素子。
8. 前記化合物と前記化合物の異性体において、長波長を発光しうる異性体と該異性体より短波長を発光しうる異性体とのモル比が、90：10～60：40であることを特徴とする請求項7に記載の有機エレクトロルミネッセンス素子。
9. 一般式〔17〕示される化合物と一般式〔18〕で示される化合物の異性体のモル比が、90：10～60：40であることを特徴とする請求項7に記載の有機エレクトロルミネッセンス素子。
10. 下記一般式〔1〕～〔18〕のいずれかで表される新規化合物。



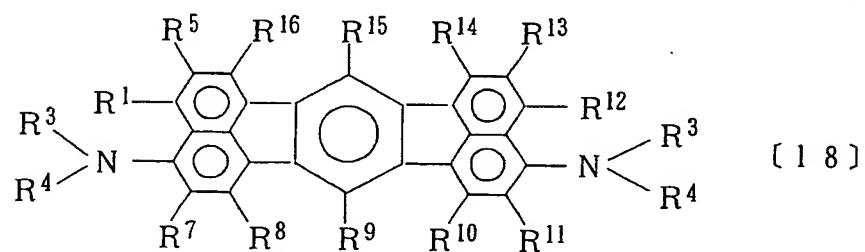
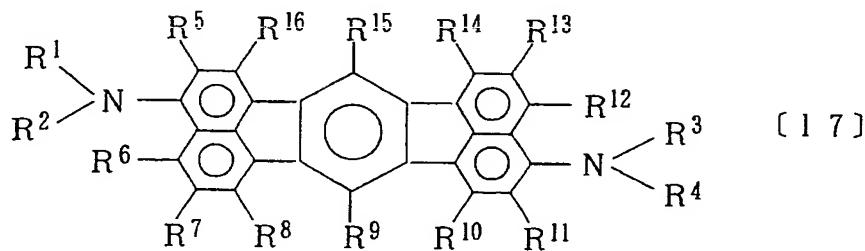






[一般式〔1〕～〔16〕式中、X<sup>1</sup>～X<sup>20</sup>は、それぞれ独立に、水素原子、直鎖、分岐もしくは環状の炭素原子数1～20のアルキル基、直鎖、分岐もしくは環状の炭素原子数1～20のアルコキシ基、置換もしくは無置換の炭素原子数6～30のアリール基、置換もしくは無置換の炭素原子数6～30のアリールオキシ基、置換もしくは無置換の炭素原子数6～30のアリールアミノ基、置換もしくは無置換の炭素原子数1～30のアルキルアミノ基、置換もしくは無置換の炭素原子数7～30のアリールアルキルアミノ基又は置換もしくは無置換炭素原子数8～30のアルケニル基であり、隣接する置換基及びX<sup>1</sup>～X<sup>20</sup>は結合して環

状構造を形成していてもよい。隣接する置換基がアリール基の時は、置換基は同一であってもよい。ただし、各式中の置換基  $X^1 \sim X^i$  ( $i = 1, 2 \sim 20$ ) の少なくとも一つはアミン又はアルケニル基を含有する。]



[一般式 [17] ~ [18] 式中、 $R^1 \sim R^4$  は、それぞれ独立に、炭素原子数 1 ~ 20 のアルキル基、置換もしくは無置換の炭素原子数 6 ~ 30 のアリール基であり、 $R^1$  と  $R^2$  及び／又は  $R^3$  と  $R^4$  は、炭素—炭素結合又は—O—、—S—を介して結合していてもよい。 $R^5 \sim R^{16}$  は、水素原子、直鎖、分岐もしくは環状の炭素原子数 1 ~ 20 のアルコキシ基、置換もしくは無置換の炭素原子数 6 ~ 30 のアリール基、置換もしくは無置換の炭素原子数 6 ~ 30 のアリールオキシ基、置換もしくは無置換の炭素原子数 6 ~ 30 のアリールアミノ基、置換もしくは無置換の炭素原子数 1 ~ 30 のアルキルアミノ基、置換もしくは無置換の炭素原子数 7 ~ 30 のアリールアルキルアミノ基又は置換もしくは無置換炭素原子数 8 ~ 30 のアルケニル基であり、隣接する置換基及び  $R^5 \sim R^{16}$  は結合して環状構造を形成して

いてもよい。ただし、各式中の置換基R<sup>5</sup>～R<sup>16</sup>の少なくとも一つはアミン又はアルケニル基を含有する。】

図 1

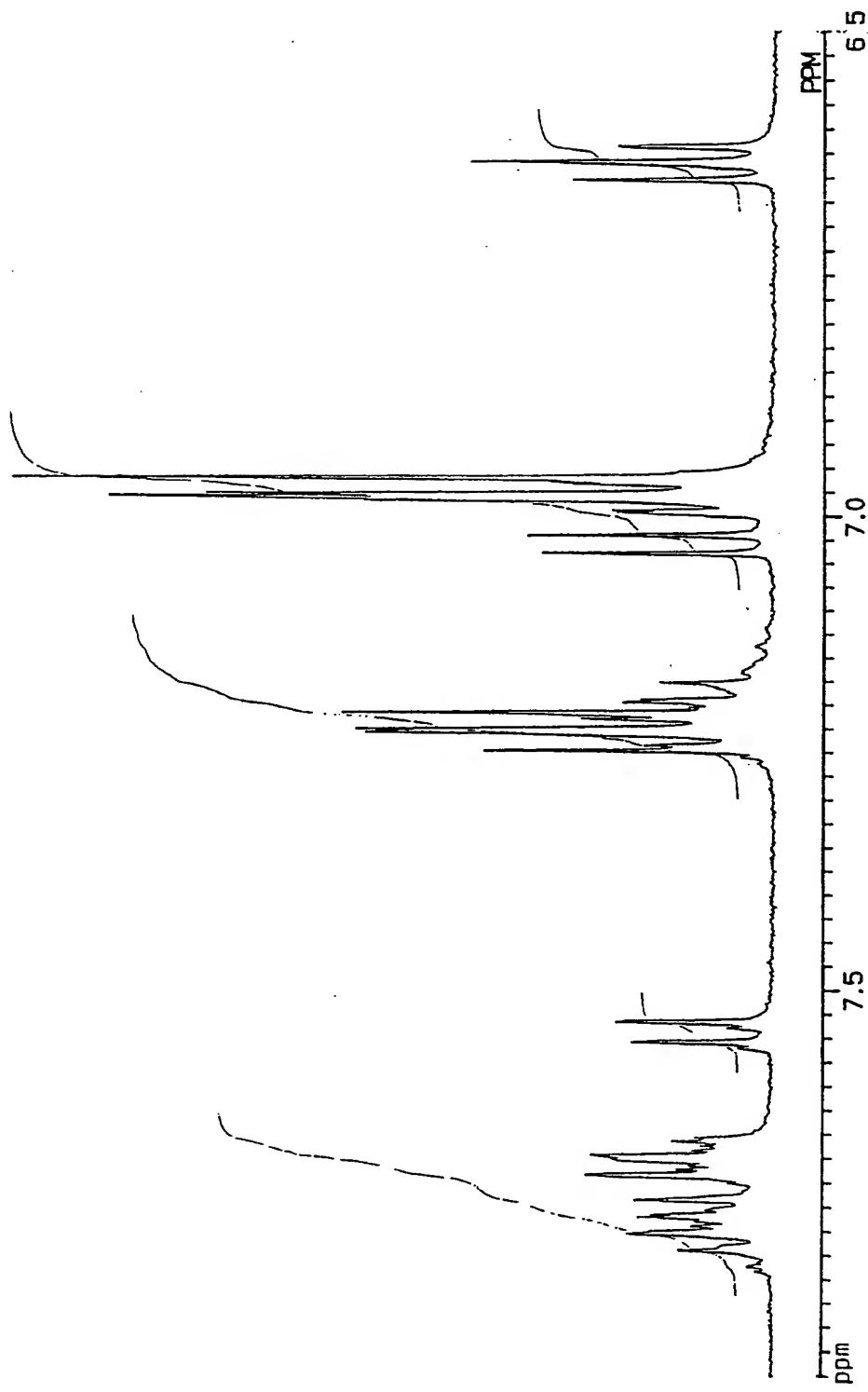


FIG 2

